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Collaborative Test of the TGS-ANSA Method for Measurement of Nitrogen Dioxide in Ambient Air

Midwest Research Inst, Kansas City, Mo

Prepared for

National Environmental Research Center, Research Triangle Park, N C Quality Assurance and Environmental Monitoring Lab

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A report on the collaborative test, by 10 organizations, of the "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA Procedure)" to determine the precision and bias of the method. The report covers the NO_2, ambient-air sampling system, test site, selection of collaborators, statistical design, collaborators' field sampling, their analysis of samples, statistical analysis of collaborators' results, conclusions and recommendations.

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COLLABORATIVE TEST OF THE TGS-ANSA METHOD FOR MEASUREMENT OF NITROGEN DIOXIDE IN AMBIENT AIR

by

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WASHINGTON, D.C. 20460

September 1974

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FOREWORD

This program, "Collaborative Testing of Methods for Measurement of NO_2 in Ambient Air," is being conducted under the Environmental Protection Agency (EPA) Contract No. 68-02-1363, which is Midwest Research Institute's (MRI's) Project No. 3823-C. The program is concerned with the evaluation of the following four methods with regard to their precision and accuracy:

1. Sodium-Arsenite,
2. TGS-ANSA,
3. Continuous-Saltzman, and
4. Chemiluminescence.

The collaborative study covered by this two-volume report is of the TGS-ANSA procedures, which is a tentative manual method. In summary, MRI's responsibility was to develop an NO_2, ambient-air sampling system for use with the four methods, provide the test site and facilities thereon where the collaborative tests would be conducted, select the collaborators with regard to the program, prepare a plan of test for the collaborative test, schedule testing, coordinate the test, retrieve field data and results from the collaborators' analysis of their samples, statistically analyze their results, and report its findings to EPA. The 10 collaborators who participated in the TGS-ANSA collaborative test are:

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Division of Air Pollution
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This volume, Volume 1 of the report of test, summarizes MRI's and the collaborators' activities. It describes the development of the NO_2, ambient-air sampling system, which covers the general concept of the system, design considerations, the design of the system and the system checkout. Following this, there are discussions on the test site, the selection of collaborators, the formal statistical design including the presentation of factors and parameters that were considered, the collaborators' field sampling at the test site, the collaborators' analysis

of their samples--both test and standard samples--MRI's statistical analyses of the collaborators' results, conclusions and recommendations. Appendices contain a copy of the tentative, TGS-ANSA method, information on the permeation tubes prepared for this program by the National Bureau of Standards, written communiques with collaborators, instructions for collaborators, and MRI's field, operational, and data-log sheets.

Volume 2 of this report of tests contains only the collaborators' field data sheets for the four-run, 240-test sample, collaborative test.

The following individuals of the collaborating organizations are acknowledged for their excellent work in the TGS-ANSA collaborative test:

California Department of Health
Mr. Kenneth Smith, field sampling and laboratory analysis

City of Philadelphia
Mr. Donald Kutys, field sampling and laboratory analysis

Kennecott Copper Corporation
Mr. Lynn Hutchinson, field sampling and laboratory analysis

Kentucky Division of Air Control
Mr. Joe Andrews, field sampling and laboratory analysis

Mecklenburg County Department of Public Health (North Carolina)
Mr. James T. Ward, field sampling and laboratory analysis

National Bureau of Standards
Mr. Bob Deardorff, field sampling and laboratory analysis

North Ohio Valley Air Authority
Mr. Dan Zorbini, field sampling and laboratory analysis

San Bernardino County Air Pollution Control District
Dr. C. Kenneth Wilcox, field sampling and laboratory analysis

Shell Development Company
Mr. W. T. Shebs, field sampling and laboratory analysis

State of New York Department of Health
Ms. Barbara Kladatos, field sampling and laboratory analysis

Special acknowledgements are made to the National Bureau of Standards and to Mr. Ernest E. Hughes and Dr. John K. Taylor of NBS who provided the NO_2 permeation tubes for this collaborative test; and to Dr. John B. Clements, Chief, Methods Standardization Branch, National Environmental Research Center, Environmental Protection Agency, and Mr. John H. Margeson, Government Project Officer, Methods Standardization Branch for their valuable suggestions in planning and design.

This MRI collaborative program is being conducted under the management and technical supervision of Mr. Paul C. Constant, Jr., Head, Environmental Measurements Section of MRI's Physical Sciences Division, who is the Program Manager. Those who contributed to this test are: development of the NO_2, ambient-air sampling system - Dr. Chatten Cowherd, Jr., Mr. Fred Bergman, Mr. Emile Baladi, and Mr. Wallace Yocum; experimental design and statistical analysis - Mr. Michael C. Sharp; and preparation and operation of test facilities - Dr. George W. Scheil, Mr. John LaShelle, Mr. Robert Stultz, Mr. Bob Kamerman, and Mr. Kevin Cline.

Approved for:

MIDWEST RESEARCH INSTITUTE

H. M. Hubbard, Director
Physical Sciences Division

17 January 1975

CONTENTS

	Page
Foreword	iii
List of Figures	ix
List of Tables	xi
Summary	xii
Introduction	1
NO_2, Ambient-Air Sampling System	3
General Concept	3
Design Factors	4
System Design	7
System Checkout	19
Ambient Levels of NO and NO_2	19
Subsystems and Units	20
System Operation	21
Test Site	23
Selection of Collaborators	29
Statistical Design	33
General Considerations and Comments	33
The Formal Design	35
Collaborators' Field Sampling	37

CONTENTS (Concluded)

	Page
Analyses of Samples	41
Analyses Performed by the Collaborators	41
Collaborators' Results	43
Statistical Analyses of Collaborators' Results	45
Biases	47
Precision	49
Summary and Discussion of Statistical Analysis	51
Lower Detectable Limit (LDL)	53
Conclusions	55
Recommendations	57
Appendix A - Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA Procedure)	59
Appendix B - Data on the Permeation Tubes Used as the Source of the Spiked Levels of NO_2	73
Appendix C - Calibration of the Venturi and Dry-Gas Meter	75
Appendix D - Written Communications with Potential Collaborators	79
Appendix E - Instructions for Collaborators NO_2 Collaborative Test: Method TGS-ANSA Procedure	85
Appendix F - NO_2, Ambient-Air Sampling System Operation Data: Test Log Sheets and Test Data Sheets	97
Appendix G - Collaborators' Comments	111
Appendix H - Analysis of Variance Including Collaborator I	117

FIGURES

Figure		Page
1	NO_2, Ambient-Air Sampling System Concept	5
2	Final Design of the NO_2, Ambient-Air Sampling System . . .	8
3	Annotated Photographs of the NO_2, Ambient-Air Sampling System in Operation	9
4	Ambient-Air Stream Splitter	11
5	Photographs of the NO_2 Bleed-In Unit--Assembled and Diassembled	14
6	Schematic Drawing of the NO_2 Permeation Tube Assembly . .	15
7	Schematic Drawing and Photographs of the Diffuser	17
8	Schematic Drawing and Photographs of the Sampling Manifold	18
9	Collaborative Test Site: MRI's Field Station	24
10	Photographs of the Test Facility	25
11	Collaborators' Sampling Areas at the Test Site	26
12	Photograph of Field Personnel of the NO_2 Collaborative Test (TGS-ANSA Method); MRI Field Station; April 29 - May 3, 1974	38

FIGURES (Concluded)

Figure		Page
13	Nitrogen Dioxide Data Sheets--TGS-ANSA Method	40
14	Collaborator Percent Bias Versus Level of NO_2	50
C-1	Venturi and Dry-Gas Meter Calibration System	77

TABLES

Table		Page
1	Sodium-Arsenite Collaborative Test Schedule	37
2	Collaborator Results from Collaborative Test Using the TGS-ANSA Method	42
3	$\bar{R}$ Versus NO_2 Level	47
4	Analysis of Variance (Response = Bias)	47
5	Average Bias ($\mu g/m^3$) Per NO_2 Level	48
6	Collaborator Biases ($\mu g/m^3$) (All NO_2 Levels)	48
7	Collaborator Percent Bias Per NO_2 Level	49
8	Components of Variance (All NO_2 Levels)	49
F-1	Run No. 1 Test Data	99
F-2	Run No. 2 Test Data	100
F-3	Run No. 3 Test Data	101
F-4	Run No. 4 Test Data	102

SUMMARY

A collaborative test was conducted by MRI in the Greater Kansas City Area during the week of 29 April 1974. Ten organizations participated in this test of the "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA Procedure)." All collaborators sampled simultaneously from the NO_2, ambient-air sampling system that was developed by Midwest Research Institute specifically for this collaborative test program. For each of the four 24-hr runs (each of a different average NO_2 level: 65.6, 117, 223, and 315 $\mu g/m^3$), each collaborator drew six samples simultaneously; four from the NO_2-spiked section and two from the unspiked (ambient-air) section of the sampling system. Each collaborator was given, for analysis with his test samples, three standard samples (two NO_2 and one blank) that were prepared by MRI.

The NO_2 challenge (spike) levels were obtained from permeation tubes that were developed by the National Bureau of Standards.

The collaborators analyzed the test and the standard samples at their home laboratories, and submitted their results to MRI. MRI checked the collaborators' calculated results and found no gross errors. The collaborators' results were then statistically analyzed.

The collaborators sampled from both the spiked and unspiked lines of the NO_2, ambient-air sampling system, providing two sets of collaborators' results. The two sets of results were used to determine true values of the levels of NO_2 that comprised the challenges to the collaborators' sampling trains. In addition, for both sets of results, there was an analysis of variances made to determine biases and components of variances--the variances of repeated observations and variances between collaborators.

The bias to the NO_2 determinations was relatively small--approximately 5%--and it was independent of the NO_2 level.

Three methods of estimating the lower detectable limit (LDL) were used. From the results of these calculations, it is reasonable to state that the LDL within a collaborator is probably ≤ 9 $\mu g/m^3$, and the LDL from a set of collaborators ≤ 15 $\mu g/m^3$.

The major conclusions that can be drawn from the results of this collaborative test are:

1. The NO_2, ambient-air sampling system developed by MRI is an effective system for use in collaborative testing of manual methods such as the TGS-ANSA procedure.

2. The "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA Procedure)" is adequately written for those knowledgeable of sampling and analysis techniques as presented therein.

3. If the tentative TGS-ANSA procedure as given in Appendix A of this report is followed by people knowledgeable of the sampling and analysis techniques given therein, then such a person will obtain results with an average bias of 9.5 $\mu g/m^3$ over the range 50-300 $\mu g/m^3$. The precisions can be estimated from the within laboratory standard deviation (σ_e) of 7.5 $\mu g/m^3$, and the collaborator standard deviation (σ_c) of 8.8 $\mu g/m^3$.

Based upon the conclusions that have been drawn from the results of this collaborative test, it is recommended that:

1. The same NO_2 sampling system be used in the evaluation of the remaining NO_2 methods to be tested;

2. The data sets to be obtained from the subsequent methods to be evaluated be based on experimental designs, test procedures and sampling system operational procedures as similar as possible to those of the TGS-ANSA collaborative test so that comparisons of the methods are based on similar criteria; and

3. No further statistical analysis be made of the results from the TGS-ANSA method until the results from the other three methods are obtained.

INTRODUCTION

The Methods Standardization Branch, National Environmental Research Center of the Environmental Protection Agency (EPA) is engaged in a program to evaluate four methods for measuring NO_2 in ambient air. Midwest Research Institute (MRI) is working for EPA under Contract No. 68-02-1363 to provide EPA data on the precision and bias of the following four methods: sodium-arsenite and TGS-ANSA, which are manual methods, and continuous-Saltzman and chemiluminescent, which are instrumental methods.

To achieve this objective, a collaborative testing program is being conducted that will assess interlaboratory as well as intralaboratory testing. In summary, MRI in the execution of this program, selects the collaborators, provides sampling locations and facilities thereon, orients the collaborators relative to the program, prepares a plan of test for each method tested, schedules testing, coordinates the collaborative tests, retrieves field data and results of the collaborators' chemical analyses of their field samples, statistically analyzes results received from the collaborators, and reports results of the program to EPA.

These activities were performed by MRI on its second test undertaken on the contract. The method investigated was the "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA Procedure)," dated April 1974. A copy of the write-up of this method is given in Appendix A.

The program was initiated on 30 June 1973, and this collaborative test took place at MRI's field station in Kansas City, Missouri, during 29 April - 3 May 1974, with 10 different collaborators. The interim period was devoted to the preparation for this test and conduction of the first collaborative test, which covered the sodium-arsenite procedure. A major task of the preparation activity was the development of a precise NO_2, ambient-air sampling system that could be housed indoors and be suitable for all four methods.

The two major phases of the test program were sampling and analysis. The sampling phase covered the field test where the collaborators collected their samples from the ambient-air sampling system. The analysis phase covered the chemical analyses of field samples by the collaborators and the statistical analyses of their results by MRI. After the field test, the collaborators returned to their home laboratories where they analyzed their samples and reported their results to MRI. Then MRI performed its statistical analysis and prepared this report of the TGS-ANSA collaborative test.

This report covers the collaborative test of the tentative TGS-ANSA method in the following order: the second section discusses the NO_2, ambient-air sampling system MRI developed for this program, covering the general concept of the system, the design considerations, the system design, and the system checkout. The third section describes the test site and the facilities that were used at this site. The fourth discusses how the collaborators were selected and who they are. The fifth section presents the factors and parameters that were considered in the formal experimental design as well as the formal design. The sixth section summarizes the test activities during the collaborative test. The seventh section discusses the analyses that were performed by the collaborators. The collaborators' results are presented in this section as well as the analysis MRI conducted. The eighth section discusses the statistical analysis of the collaborators' results and presents the results from this analysis, which includes biases and components of variance. The ninth and tenth sections present conclusions and recommendations, respectively. The appendices contain a copy of the tentative TGS-ANSA Procedure method, data on the permeation tubes that were used as the source of NO_2 in the spiked section of the sampling system, information concerning the calibration of the venturi and dry-gas meter, copies of written communiques MRI had with the collaborators, a copy of the test instructions that were given to the collaborators, the NO_2, ambient-air sampling system's operational data, collaborators' comments, results of MRI's analyses, and additional statistical-analysis information.

NO_2, AMBIENT-AIR SAMPLING SYSTEM

GENERAL CONCEPT

Primary requirements for the evaluation of an ambient-air method by on-site collaborative testing are: (1) that all collaborators sample the same air, (2) that the samples be representative of ambient air, and (3) that the concentration of NO_2 in the samples be accurately known and controllable over the region of interest. The first requirement can be met by using a manifold system with each collaborator taking samples from a common stream of air. The second and third requirements are somewhat antagonistic to one another and not as easily solved.

Ideally, these requirements can be met by obtaining actual ambient samples over a wide range of concentration. However, this approach would require that each level be obtained at a different location with the additional requirement of fortuitous weather conditions, since weather conditions have a strong effect on ambient NO_2 concentrations. An additional problem with this approach is that no accepted primary reference method exists for the analysis of NO_2 in ambient air.

However, gravimetrically calibrated NO_2-permeation tubes are available which generate a stable, precise rate of release of high purity NO_2 over a period of a few years. By using a set of these tubes different levels of NO_2 can be generated by adding the NO_2 from the permeation tubes to a stream of air with a known flowrate. Since the test conditions must relate to actual ambient-air conditions, the NO_2 from the permeation tube can be added as a known addition or spike to the ambient air stream. The method under test should show a difference in concentration between samples of ambient and spiked air equal to the spike level. To ensure that the NO_2 concentration of the spiked sample does not exceed the maximum level of interest--350 $\mu g/m^3$--and to allow control of the spiked air NO_2 level over a reasonably broad range, the average ambient levels must be well below the lowest NO_2 concentration to be tested, in this case 50 $\mu g/m^3$.

To achieve this, the following system is used: outdoor ambient air is drawn into the sampling system through a single tube, as shown in Figure 1. The air is divided downstream into two sections--spiked and unspiked. A controlled flow of ambient air at a specific value exists in the spiked section. A comparable ambient-air flow exists in the unspiked section, but the latter is uncontrolled. Temperature-controlled permeation tubes provide the source of NO_2 which is injected into the spiked section at a desired level. The NO_2 is then thoroughly mixed with the ambient air in a mixing unit--a diffuser. The mixture is then equilibrated before it reaches the sampling station where the collaborators sample from identical ports--subjected to the same gas flow (spiked plus ambient). A continuous monitor is attached to monitor the gas at the spiked and unspiked sampling levels to monitor the integrity of the spike. The collaborators sample ambient air simultaneously at an identical sampling manifold that is at a similar location in the unspiked section. The gas in both sections is then exhausted to the outdoors.

DESIGN FACTORS

The design of the NO_2, ambient-air sampling system was based on the following factors:

1. The flowrate of each of the four methods to be tested is approximately 0.2 liter/min, with a maximum of 1 liter/min for some of the instruments that would be used in the instrumental methods.

2. The sampling period of each manual method is 24 hr; each instrumental method is preferably 24 hr, but could be less.

3. NO_2 permeation tubes whose rates are approximately 1 μg/min, which are furnished by the government, are the source for the spiked levels of NO_2. These tubes are to be operated at 25.1°C ± 0.2°C.

4. The number of collaborators for each collaborative test is to be 10.

5. The maximum number of samples taken simultaneously by each collaborator during each run of a manual method is four spiked and two ambient (unspiked) for a total of six samples/collaborator/run. The multiplicity of samples per run--both spiked and unspiked--is to provide replicates.

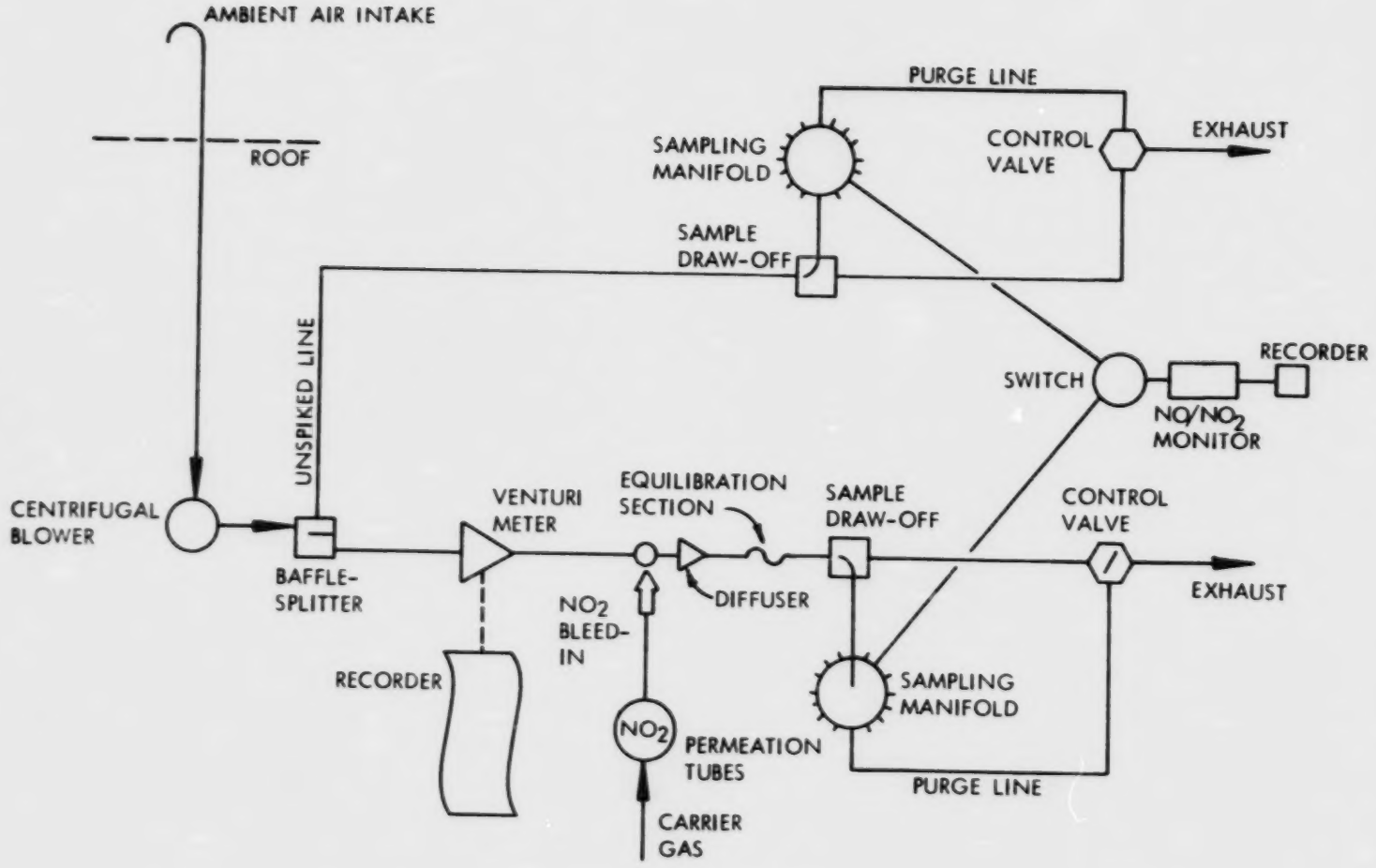


Figure 1. NO_2, ambient-air sampling system concept

6. The NO_2 range of concern is 50-350 $\mu g/m^3$, which is representative of ambient conditions.

7. There are four different NO_2 spiked levels: high, low, and two medium. Each level is maintained throughout the run's period, within the accuracy of the system.

8. The test period is to be no more than 6 days, which is based upon the concensus of potential collaborators surveyed.

9. The overall NO_2 sampling system accuracy is to be 5% or better.

10. The flow control in the spiked section is to be 2% or better.

11. Flow parameters of the spiked section are to be measured.

12. One NO_2/NO chemiluminescent device, switched between spiked and unspiked sampling manifolds (or stations), is to be used as a monitoring instrument.

13. Only one person from each collaborators' organization will be needed in the field for each method.

14. There is turbulent flow in the spiked section between the point of injection of the spiked levels of NO_2 and the diffuser to provide mixing of the spiked NO_2 with the ambient air. The diffuser insures proper mixing. Up to 20% of the stream in each section--spiked and ambient air--can be sampled to (a) insure that there is capacity in the main stream to provide each collaborator with his needs in case there is a problem with one or more collaborators drawing an excess amount, and (b) allow the quantity of spiked flow to be drawn from the center of the spiked line where there is assurance of equilibration. There is to be a minimum amount of adsorption of the spiked NO_2 on surfaces, from its source to and including the sampling manifold. By using Teflon or glass as the material in which the gases come in contact and by maintaining a high gas flowrate, which allows for extremely short residence times, adsorbtivity of NO_2 on surfaces and reaction with water vapor and other losses are insignificant.

15. Each section--spiked and unspiked--is to be similar, including material and geometric aspects.

16. Each section is to be under positive pressure so that no unwanted air will be pulled into the system in case there were a leak.

17. Collaborator's equipment size, configuration and power requirements must be met.

18. Environmental effects on operation of sampling system must be considered.

SYSTEM DESIGN

The final design of the NO_2, ambient-air system is shown in a general schematic form in Figure 2. Annotated photographs of this operational system are given in Figure 3.

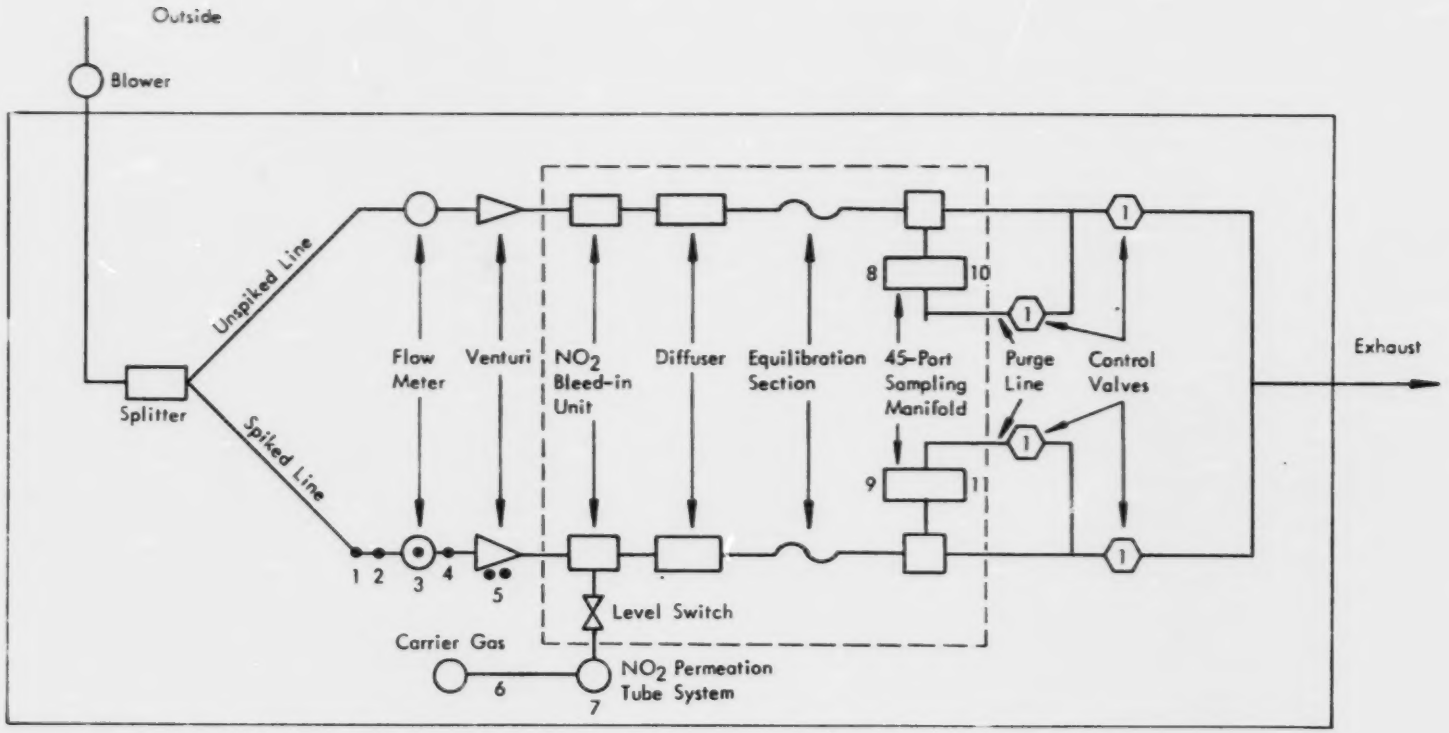
The input to the system is located outdoors about 2 m above ground level and approximately 30 m from the building. A valve at the intake of the 2-in. aluminum tubing provides resistance to the flow of ambient air to keep the Model 8700 DMP "Tornado" blower at a stable rpm, and to serve as a gross flow control. A Variac inside the building serves as an operational flow control. The blower is located at the input end of the system to provide positive pressure in the system. It is located outdoors to keep out the intensive noise it generates and is housed as shown in photographs 1 and 3 of Figure 3 to protect it from the elements.

The line from the blower to the splitter is 2-in. diameter, aluminum pipe. It is sufficiently long to serve as a trap for any excess moisture and to bring the ambient air to room temperature. The splitter is also made of aluminum. This splitter, shown in Figure 4, reduces large-scale turbulance from the blower and divides the ambient air stream between the spiked and unspiked 1-in. diameter, aluminum lines. A controlled flow goes to the venturi where the air flow in the spiked line is continuously measured and recorded. This flow is determined by the following equation:

$$\text{Flow in liters/min} = \frac{\text{method sampling rate (number of samples x number of collaborators + monitor number + purge number)}}{\text{percent flow drawn through sampling manifold}}$$

$$= \frac{0.2 \text{ liters/min x (4 samples x 10 collaborators + 1 } NO/NO_2 \text{ monitor + purge-line flow)}}{\text{percent flow drawn through sampling manifold}}$$

$$= \frac{0.2\ (4 \times 10 + 1 + 4)}{0.15} = \frac{9}{0.15} = 60$$



Monitoring Points:

1. Flow Temperature
2. Flow Pressure at Input to Flow Meter
3. Ambient Air Flow
4. Flow Temperature
5. Pressure Drop of Venturi & Temperature of Pressure Transducer
6. Carrier Gas Flow
7. NO_2 Flow Temperature
8. Port Pressure
9. Port Pressure
10. NO_2 & NO
11. NO_2 & NO

Notes:

1. Component within Dashed Area Made of Teflon
2. Piping Out Side Dashed Area made of Aluminum
3. Venturis made of Stainless Steel
4. Spiked & Unspiked Lines Symmetric with Respect to Geometry & Material

Figure 2. Final design of the NO_2, ambient-air sampling system

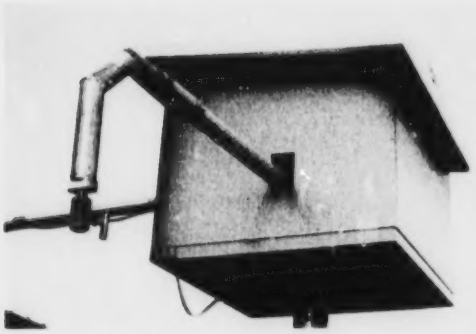


Photo 1 - Air Intake and Blower Housing. 2" Aluminum tubing. Valve on intake provides resistance to flow to keep blower at a stable rpm. Intake is 2 meters above ground level and about 6 meters from station roadway.

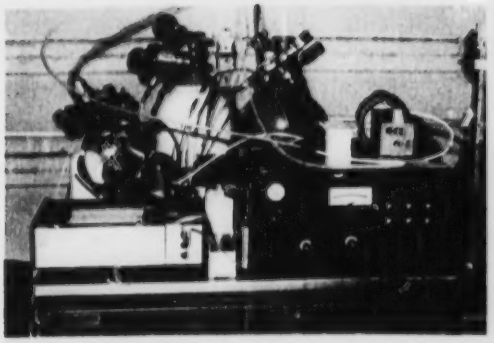


Photo 12 - Bendix Model 8101B NO-NO_2-NO_x Analyzer Used to Monitor Levels of NO and NO_2 in Spiked and Unspiked Lines.

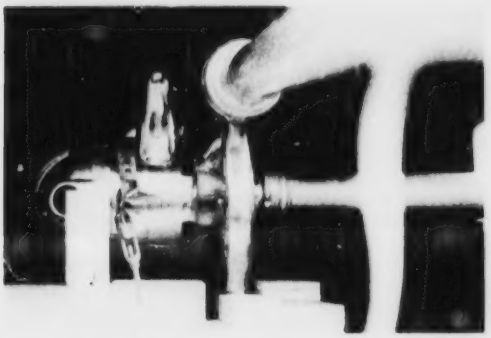
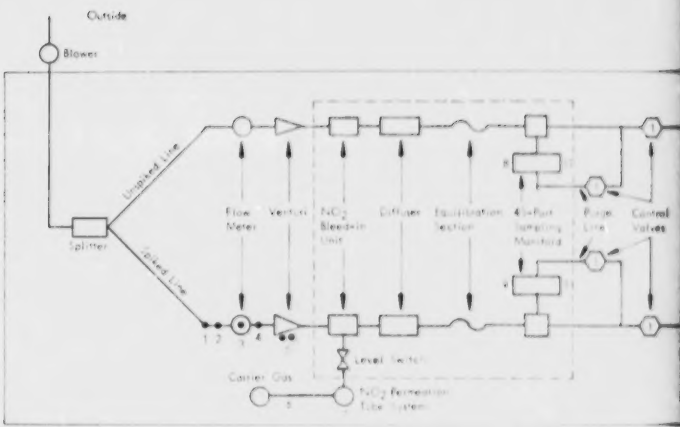


Photo 2 - Blower. Model 8700 DMP. "Tornado." Breuer Electric Company, Chicago, Illinois.



Monitoring Points:
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4. Flow Temperature
5. Pressure Drop at Venturi & Temperature at Pressure Transducer
6. Carrier Gas Flow
7. NO_2 Flow Temperature
8. Port Pressure
9. Port Pressure
10. NO_x & NO
11. NO_x & NO

Notes:
1. Components within Dashed ... Made of Teflon
2. Piping Out Side Leached A... of Aluminum
3. Venturi made of Stainless
4. Spiked & Unspiked Lines ... respect to Geometry &

(A) - General Schematic of the Ambient-Air NO_2 Sampling System

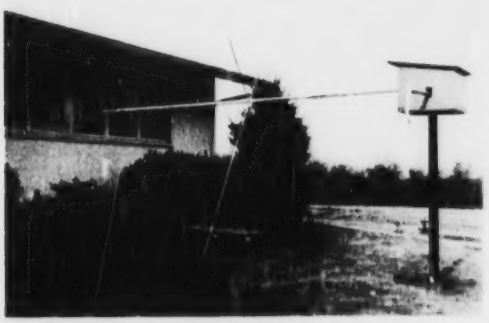


Photo 3 - Blower Housing and 2" Line Going into Building.

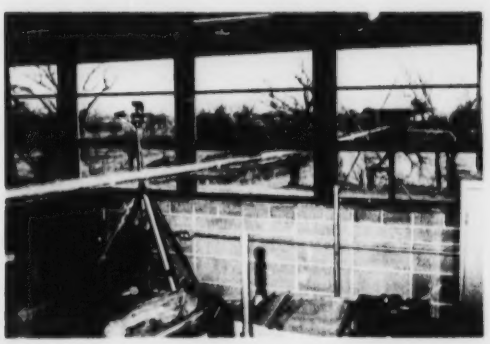


Photo 4 - View from Inside Building of Line from Blower.

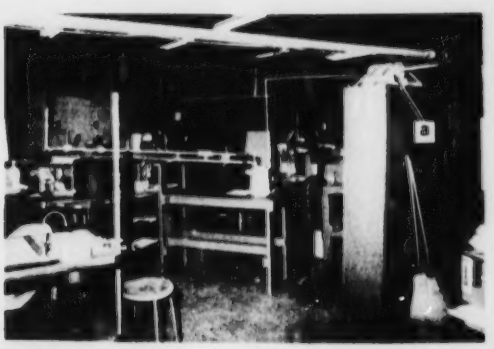
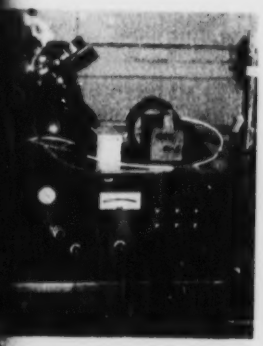


Photo 5 - 2" Aluminum Tubing Going into Splitter (a) Located on Top the Metal Cabinet--Top Right of Photo.

a

Figure 3 - Annota



NO_2-NO_x Analyser Used to Monitor ed and Nonspiked Lines.

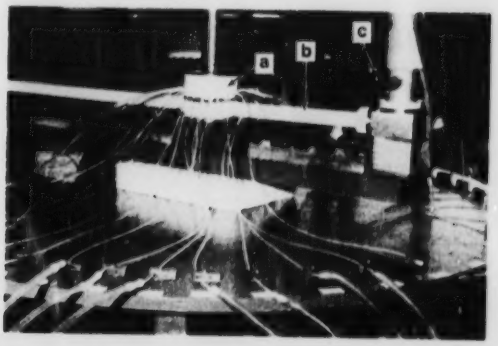


Photo 11 - Sampling Manifold (a) with Bypass Line (b) and Butterfly Control Valve (c) to Exhaust

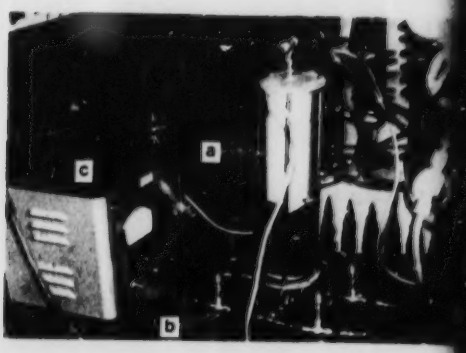
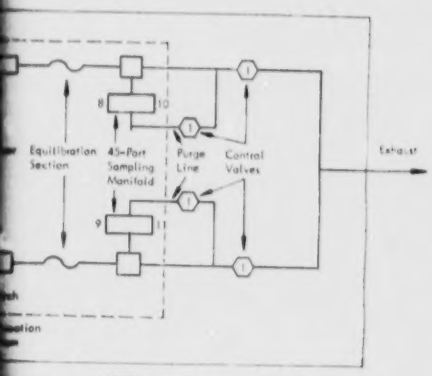


Photo 8c - Filter (a) and Contol Valve Manifold (b) on Inlet Side of Permeation Tube System. Filter body is 10-cm diam. polystyrene tube 40-cm long, with brass end caps. Stainless steel needle valves on each line going to rotameters. Capacitance relay unit (c) is connected to wire around one of the thermometer stems and turns off temperature control unit (e of Photo 8b) if both temperature exceeds 27°C.



Notes:
1. Components within Dashed Area Made of Teflon.
2. Piping Out Side Dashed Area made of Aluminum.
3. Venturis made of Stainless Steel.
4. Spiked & Unspiked Lines Symmetric with Respect to Geometry & Material.

ient-Air NO_2 Sampling System.

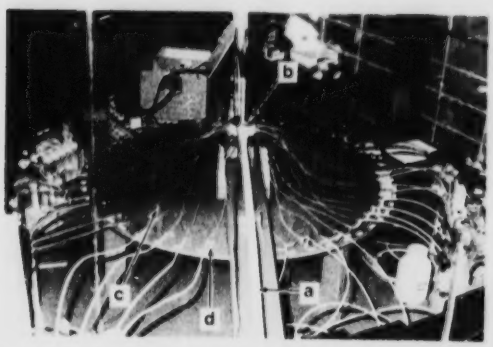


Photo 10 - 1" Teflon Pipe Equilibration Section (a) and Spiked Line Sampling Manifold (b). 1/8" Teflon tubing (c) connects manifold to the sampling ports (d) on circumference of upper table.

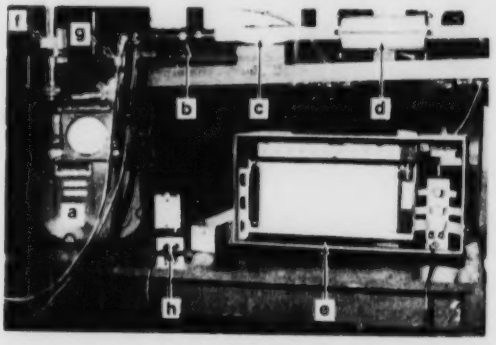
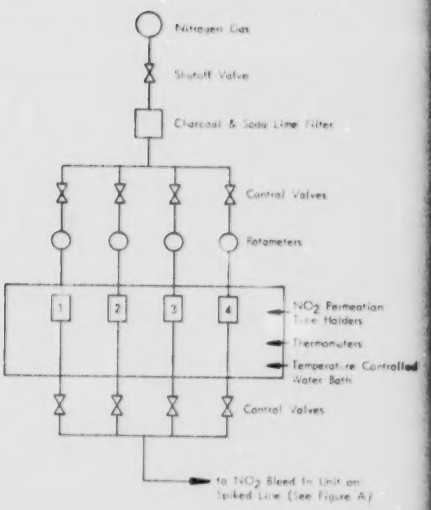
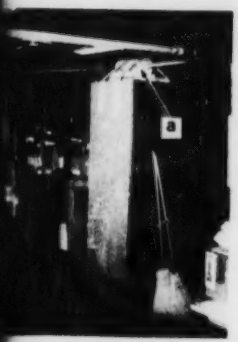


Photo 9 - Front View of Dry Gas Meter (a). Venturi (b). NO_2 Bleed-In Unit (c), and Diffuser (d). Recorder (e) is connected to thermocouples (f and g) at inlet and outlet of gas meter with switching unit (h) that alternates readings of the two thermocouples.



(8) - Block Diagram of NO_2 Permeation Tube Assembly. Various combinations of the permeation tube holders are connected to the outlet manifold to provide the different spike levels.



Splitter (a) Located on Top the

b

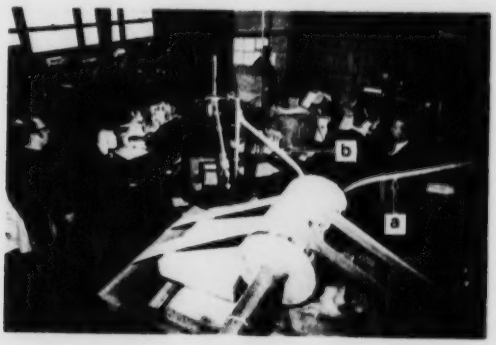


Photo 6 - Splitter with 1" Aluminum Tubing on Outlets to Spiked Line (a) and Unspiked Line (b). Internal baffles in splitter divide incoming airflow into two equal paths.

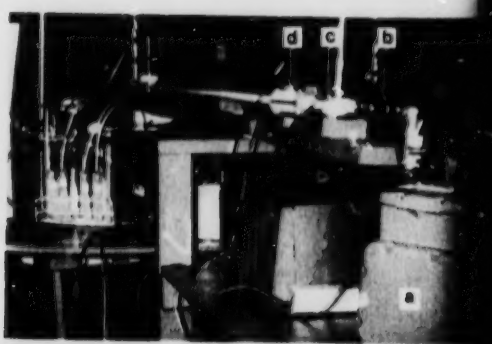
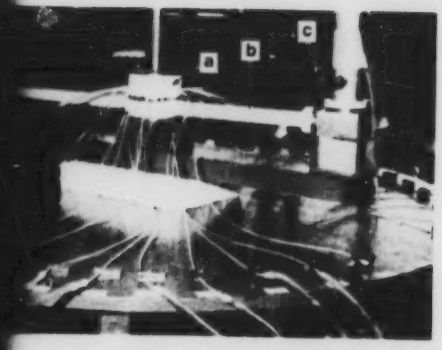


Photo 7 - Dry Gas Meter (a). Singer AL-175, American Meter Company, Stainless Steel Venturi (b). NO_2 Teflon Bleed-In Point (c), and Teflon Diffuser (d) on Spiked Line.

Figure 3 - Annotated Photographs of the NO_2, Ambient-Air Sampling System in Operation



...e 11 - Sampling Manifold (a) with Bypass Line (b) and Butterfly Control Valve (c) to Exhaust

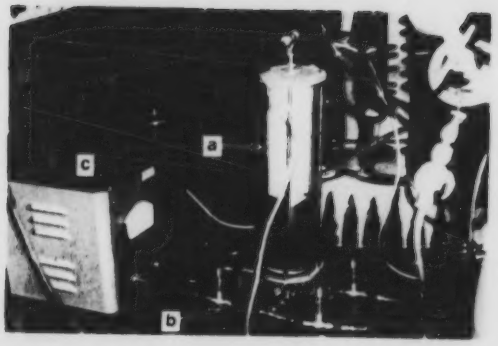


Photo 8c - Filter (a) and Contol Valve Manifold (b) on Inlet Side of Permeation Tube System. Filter body is 10-cm diam. polystyrene tube 40-cm long, with brass end caps. Stainless steel needle valves on each line going to rotameters. Capacitance relay unit (c) is connected to wire around one of the thermometer stems and turns off temperature control unit (e of Photo 8b) if bath temperature exceed 27°C.

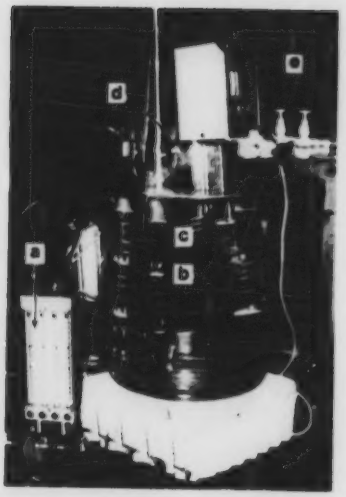
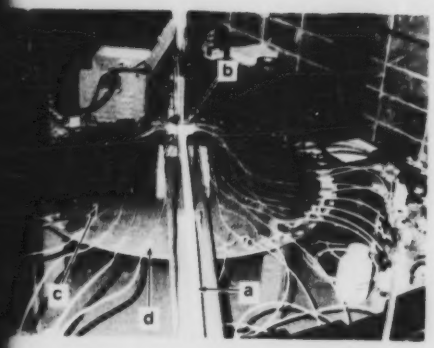
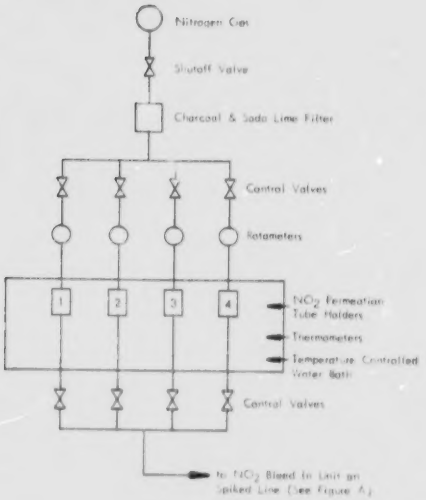


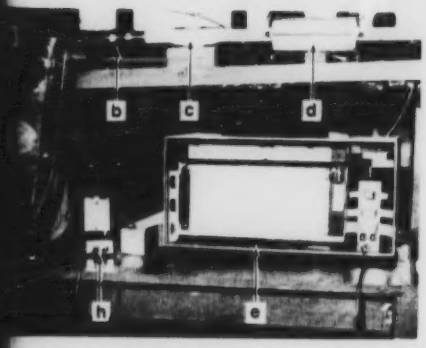
Photo 8b - Permeation Tube Bath Assembly. Tygon tubing from rotameters (a) connects to copper heat exchanger coils (b) wrapped around glass jacket (c) of each permeation tube holder. Nitrogen flow comes in at bottom, flows past the permeation tubes held by Teflon spacer disks, and outside neck at top of holders (d). ASTM 0-30° thermometers sealed into top of holders with thermometer bulbs about 4 cm below water level in bath. Temperature control/stirrer unit (e) is Model E52N, Haake Instruments, Inc., Saddlebrook, N.J.



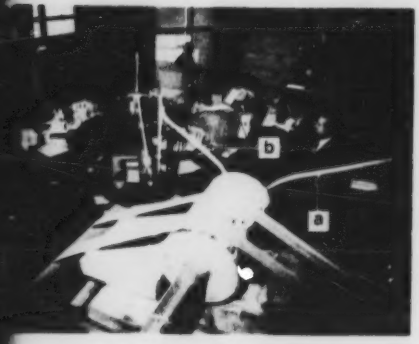
...e 10 - 1" Teflon Pipe Equilibration Section (a) and Spiked Line Sampling Manifold (b). 1/8" Teflon tubing (c) connects manifold to the sampling ports (d) on circumference of upper table.



(8) - Block Diagram of NO_2 Permeation Tube Assembly. Various combinations of the permeation tube holders are connected to the outlet manifold to provide the different spike levels.



...Front View of Dry Gas Meter (a). Venturi (b). NO_2 Bleed-In (c) and Diffuser (d). Recorder (e) is connected to thermocouples ...g) at inlet and outlet of gas meter with switching unit (f) that ...otes readings of the two thermocouples.



...Splitter with 1" Aluminum Tubing as Outlets to Spiked Line (a) ...piked Line (b). Internal baffles in splitter divide incoming ...e into two equal parts.

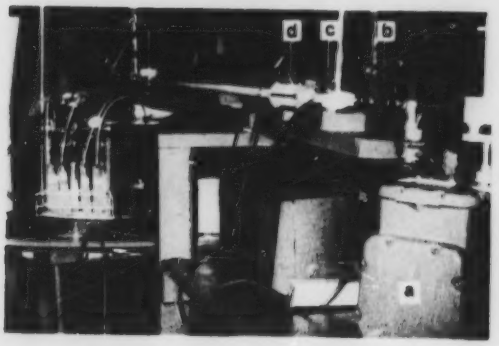


Photo 7 - Dry Gas Meter (a). Singer A1-175, American Meter Company. Stainless Steel Venturi (b). NO_2 Teflon Bleed-In Point (c), and Teflon Diffuser (d) on Spiked Line.

Photo 8a - Top View of Temperature-Controlled Water Bath and Permeation Tube Assembly with Teflon Manifold and Control Valves (Top Right) and NO_2 Feed Line to Point c of Photo 7.

NO_2, Ambient-Air Sampling System in Operation

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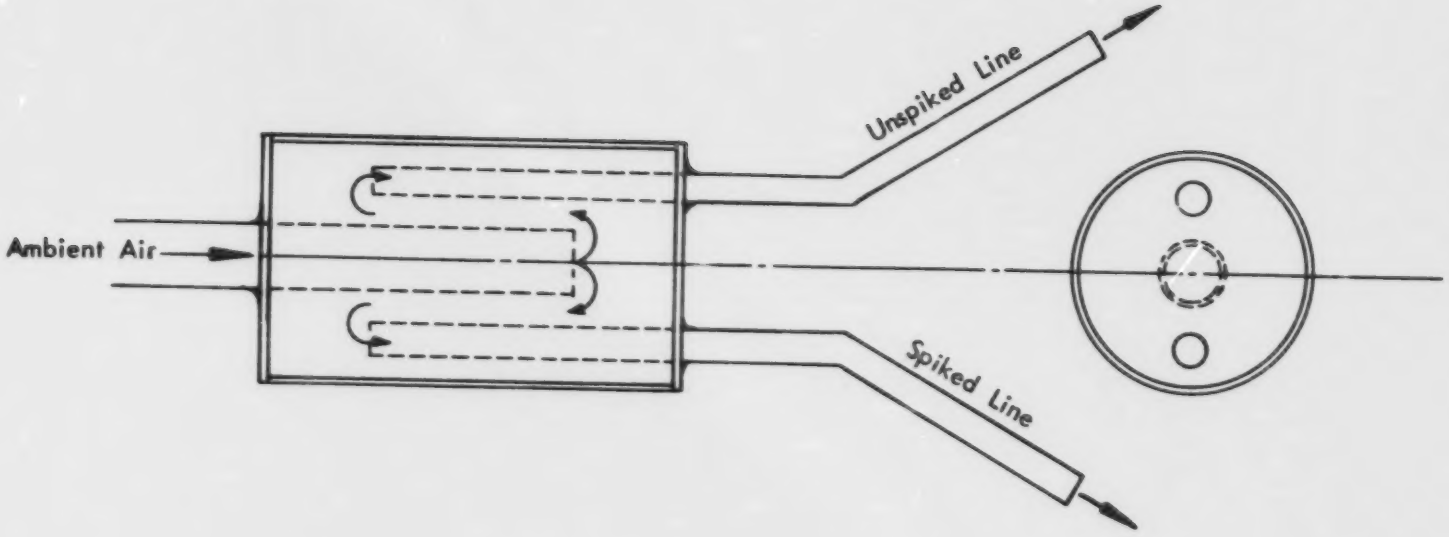


Figure 4. Ambient-air stream splitter

The monitor number and the purge number are flows attributable to the continuous monitor and the purge line of the system, respectively. The flow on each line--the spiked and the unspiked--is turbulent--Reynolds No. > 2,100--with the Reynolds number being

$$R = \frac{Q}{\alpha \nu D} = \frac{Q \text{ liter/min} \times 1{,}000 \text{ cm}^3/\text{liter}}{0.785 \times 0.15 \text{ cm}^2/\text{sec} \times D \text{ sec} \times 60 \text{ sec/min}}$$

$$= \frac{1{,}000\ Q}{7.065\ D} = \frac{1{,}000 \times 60}{7.065 \times 2.1} = 4{,}000.$$

Since the spiked and unspiked sections are identical except that the spiked section also contains the monitoring points 1, 2, 3, 4, and 5 identified in Figure 2 and the NO_2 permeation tube system, only the spiked section will be discussed.

From the splitter, the spiked line connects to a Singer AL-175 dry-gas meter, which is made by the American Meter Company. (See photograph 9 of Figure 3.) This flow meter has a pressure drop of 10 mm of water and is temperature-compensated. Thus, only the gas pressure is measured to correct the flow readings to obtain the true flowrate of ambient air delivered during a test run. This flowrate is determined hourly by measuring the time required for a known quantity of air to pass through the meter.

The output of the flow meter is connected, as shown in photographs 7 and 9 of Figure 3, to a stainless steel venturi, which was designed for a flow of 60 liters/min. This venturi is used as a general flow control device, and provides a continuous record of flowrate using a strain gage pressure transducer and thermocouples--see point 5 of Figure 3(A). Both the pressure drop of the venturi and the temperature of the pressure transducer are recorded on analog recorders. Control of the flowrate is handled by monitoring the venturi pressure drop. When the value deviates from a reference value, 60 liters/min, the flowrate can be changed appropriately by making an appropriate adjustment of the Variac control to the blower.

The flow temperature measurement (point 4 of Figure 3(A)) is actually the gas-flow temperature at the output of the gas meter and at the input to the venturi, since those two units are physically close together (about 12.5 cm apart). Tests have shown that the temperature at this point is identical with the temperature at the gas flow meter inlet. The gas temperature at this point is normally within 5°C of room temperature. This temperature measurement is used to obtain accurate gas-flow values.

To provide more accuracy, the thermocouples at points 2 and 4 of Figure 3(A) were replaced for this test by a 0-50°C bimetallic dial thermometer that is located at point 4 of Figure 3(A).

The output of the venturi is a few centimeters from the input of the NO_2 bleed-in unit as shown in photograph 9 of Figure 3. These two units are connected by 10-in. diameter, aluminum tubing. From the input of the NO_2 bleed-in unit through the sampling manifold, the system is made of Teflon.

The NO_2 bleed-in unit, as shown in Figure 3(A) and photographs 7 and 9 of Figure 3, receives ambient air from the venturi and a level of NO_2 (a spike) from the NO_2-permeation tube assembly (see Figures (A) and (B), and photographs 8 a-c of Figure 3). Detailed photographs of this bleed-in unit are given in Figure 5. Photograph 1 of Figure 5 is a closeup showing the assembled Teflon unit with its metal holding/mounting plates. The gas stream, or ambient air, enters the opening to the right and passes through the unit, mixing with the spiked level of NO_2 which exits through the tapered smaller tubing shown as concentric to the output of the bleed-in unit at the left of photograph 1 of Figure 5. The vertical tube of this bleed-in unit accepts the NO_2 gas from the permeation tube assembly. This spiked gas flows downward through this tube, which is inside the unit (see photograph 2 of Figure 5), and after a short run, mixes with the ambient air as stated before.

The NO_2-permeation system is shown in Figure 6 and photographs 8 a-c of Figure 3. Details of the system are given in the captions of these photographs. The nitrogen carrier gas is used to flush the NO_2 into the system. It is passed through a charcoal and soda-lime scrubber before it is delivered to the NO_2-permeation tubes. Also, the flow is set by means of control values and rotameters. This flow is monitored during system operation. The carrier gas is then fed into four separate branches to achieve different levels of NO_2. (More detail on the permeation tubes and their arrangements in the branches is given in Appendix B.) The NO_2-permeation tubes* are arranged in these four different branches to provide NO_2 spike levels of approximately 50, 100, 200, and 300 $\mu g/m^3$. Branch 1 has four permeation tubes, branch 2 has five permeation tubes, branch 3 has two permeation tubes, and branch 4 has two permeation tubes. An ASTM calibrated thermometer (0.1°C or better accuracy) is an integral part of

* "Operation Characteristics of NO_2 Permeation Device," by Harry L. Rook, Ernie E. Hughes of NBS, Washington, D.C., and Robert S. Fuerst and John Margeson of EPA, Research Triangle Park, North Carolina. A paper presented before the Division of Environmental Chemistry, American Chemical Society, Los Angeles, California, 31 March - 5 April 1974.

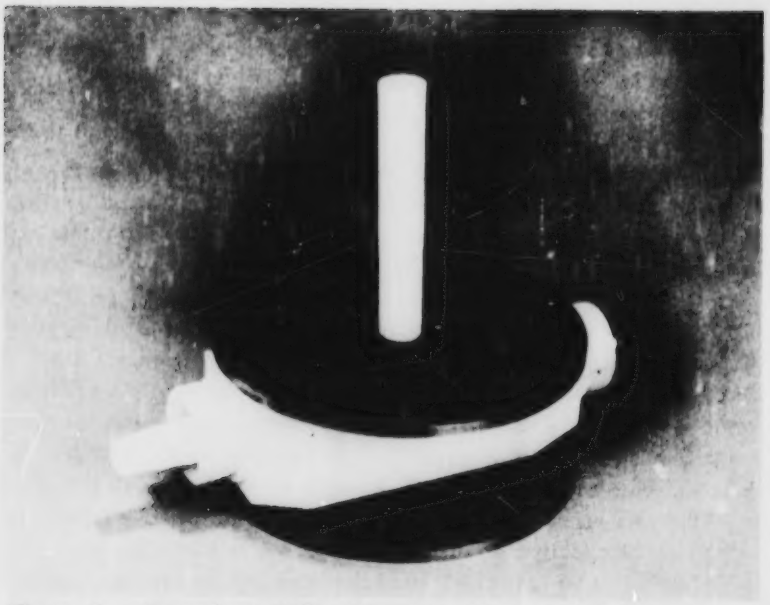


Photo 1 - Detail of NO_2 Bleed-In Unit with Vertical Tube from Permeation Assembly, Chamber with Central Tapered Pickup Tube and Stainless Steel Mounting Components.

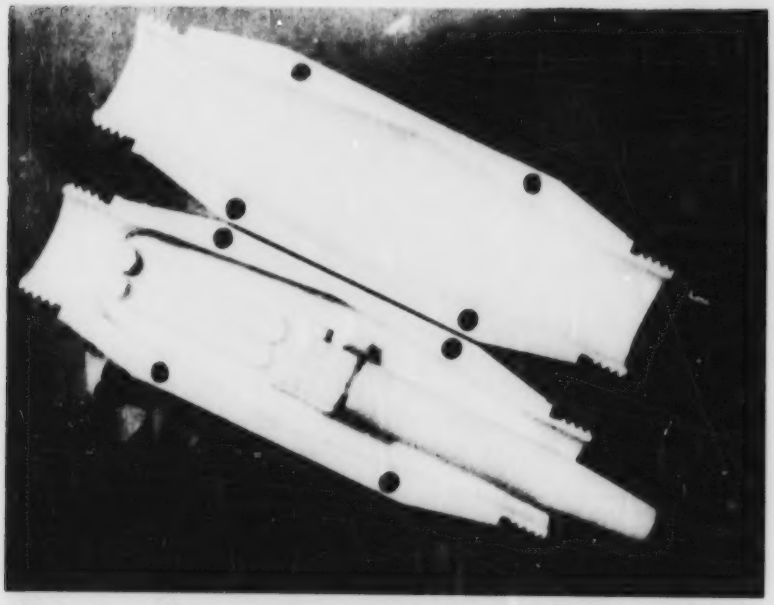


Photo 2 - Close-Up Showing Machined Chamber with Pickup for Bleed-In in Place.

Figure 5 - Photographs of the NO_2 Bleed-In Unit-- Assembled and Disassembled

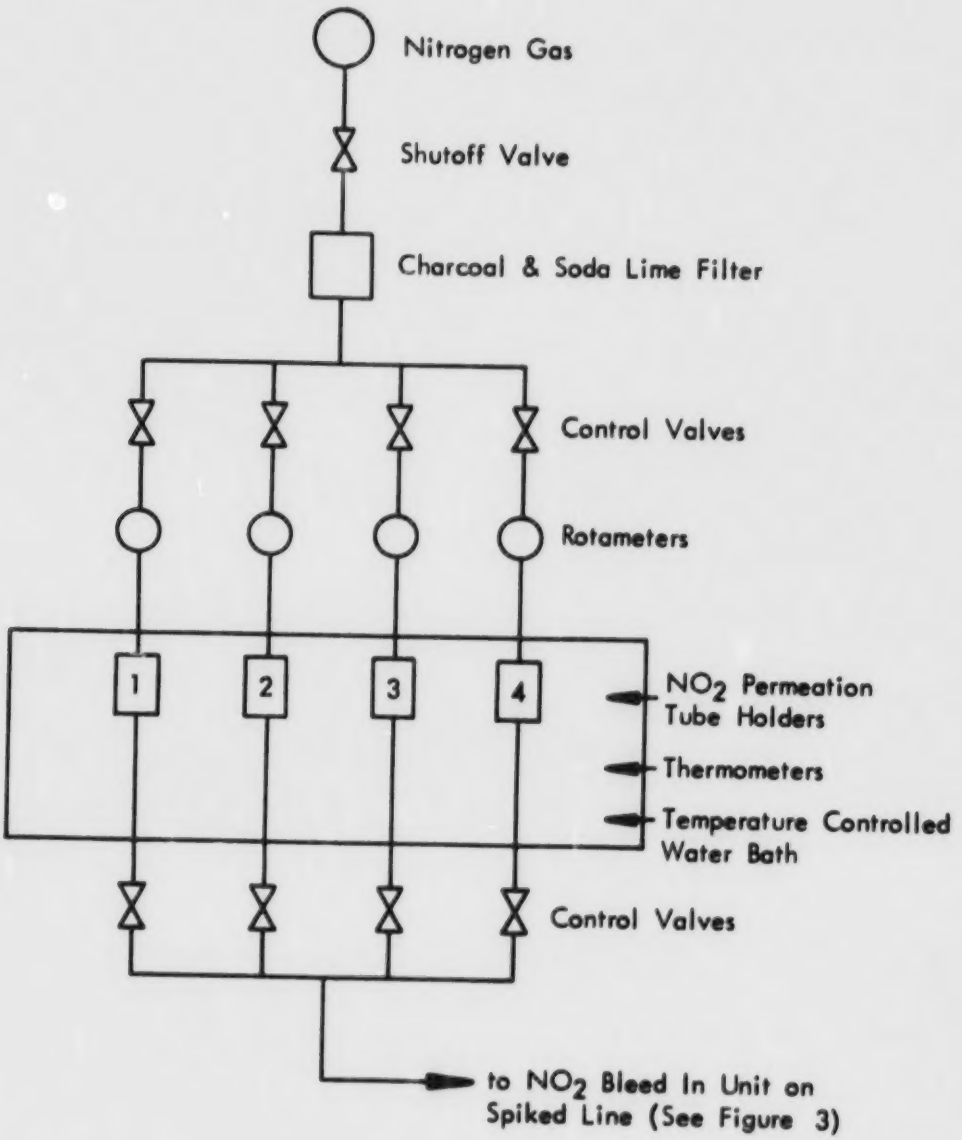


Figure 6. Schematic drawing of the NO_2 permeation tube assembly

each permeation tube branch. Each set of permeation tubes is enclosed in a glass tube which has an inlet for the nitrogen carrier gas and an outlet for the nitrogen carrier gas/NO_2 mixture. These NO_2 permeation tube, enclosure units are immersed in a temperature-controlled, water bath for operation at 25.1°C. If the temperature of this bath were to vary more than 0.2°C, a correction would be made from the following relationship:

$$\text{Log } r = 0.034857\ (273.12 + T) - 10.29198$$

where T = temperature in °C of the permeation tube environment, and
r = the permeation rate.

Flow meters of the permeation tube assembly that measure the nitrogen flow were calibrated by the manufacture to 1% accuracy. Thermometers that were used to measure the gas temperature in the permeation tube holders are ASTM type that are accurate to within 0.1°C. The permeation tubes used were calibrated by the National Bureau of Standards and checked by EPA. (See Appendix B.) The entire permeation assembly from the tube holders to the pickup fitting, where the spiked gas enters the main gas stream, was checked for leaks with Snoop and found to be airtight.

The ambient air and the NO_2 flow from the bleed-in unit to the diffuser where they are well mixed. The diffuser is a few centimeters downstream from the bleed-in unit, as shown in photograph 9 of Figure 3. At the diffuser, shown schematically and in the photograph in Figure 7, the gases enter the diffuser through the Teflon tubing (Section A of the schematic drawing of Figure 6), pass into the spiraled tube and through its angled holes into the space outside the tube. The flow continues through the holes in the prescreen block, item D of the schematic, and then through a series of Teflon screens, item E.

The homogeneous mixture passes through an equilibration section that is Teflon tubing 1.0 m long. This section of tubing provides the final equilibrated concentration. This tubing is connected to the input of the sampling manifold. (See photographs 10 and 11 of Figure 3.)

The 45-port sampling manifold is constructed of Teflon except for its metal plates which are entirely external. Photographs 1-3 of Figure 8, which show external and internal views of the sampling manifold and a schematic drawing, describe the operation of the manifold. The stream of the homogeneous mixture of ambient air and a spiked level of NO_2 flows through the bottom portion of the manifold, into the exhaust line.

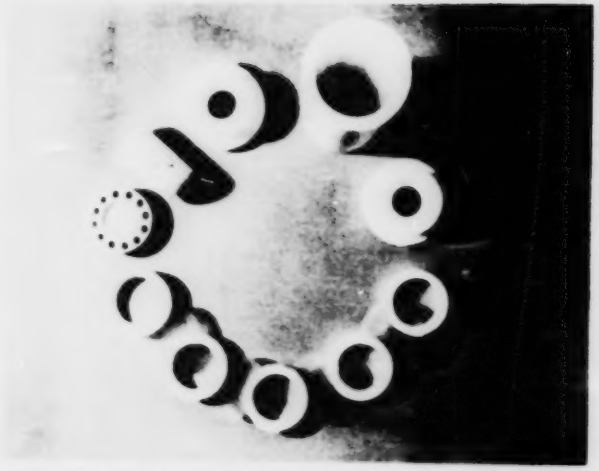


Photo 1 - Top View Diffuser Components: Housing, End Sections, Spiraler Tube, Teflon Screens, Retaining Rings.

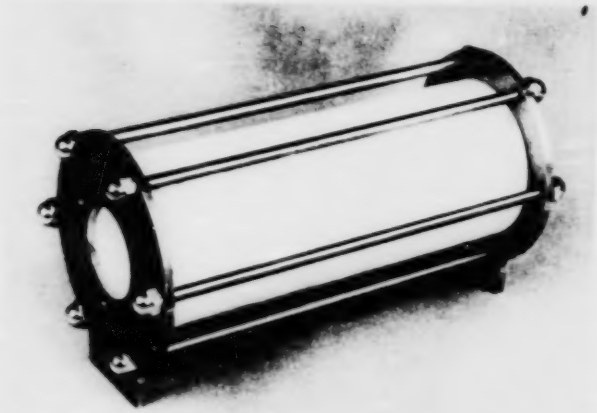
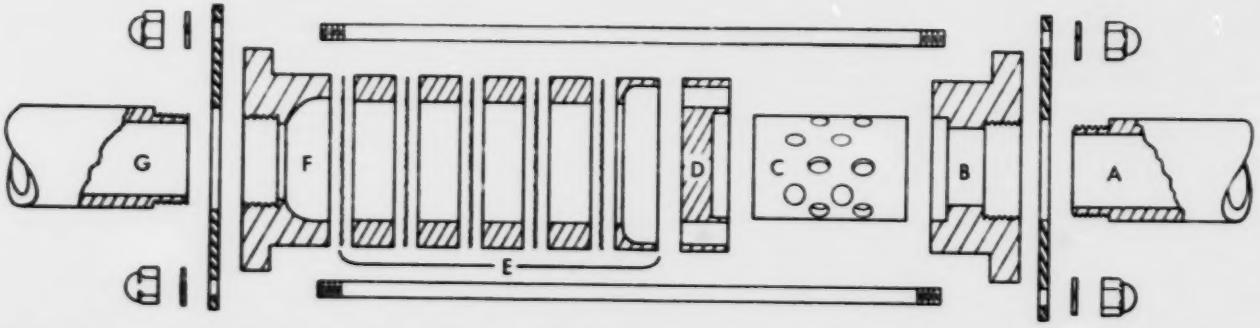


Photo 2 - External View of Diffuser.



Exploded cross section of all-Teflon diffuser with inlet (A), end section (B), spiraler tube with angled holes (C), prescreen block with holes (D), five sets of fine mesh Teflon screen and retaining blocks (E), end section (F), exit (G) and diffuser housing (H). Double cross-hatched end plates are stainless steel.

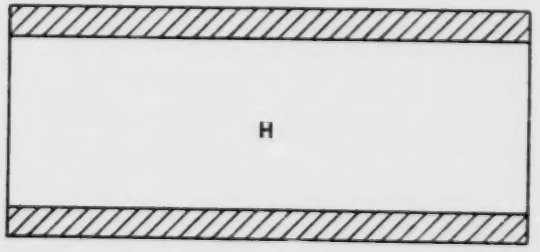


Figure 7. Schematic Drawing and photographs of the diffuser

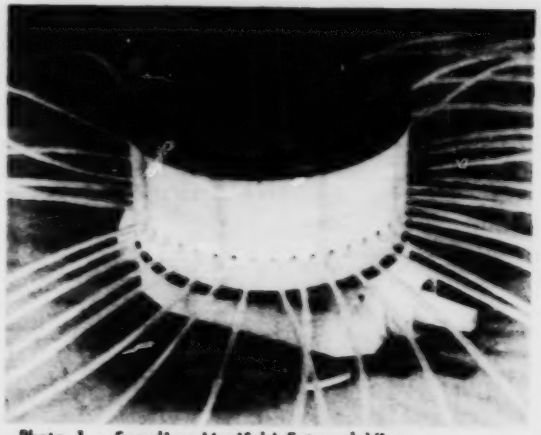


Photo 1 - Sampling Manifold External View.

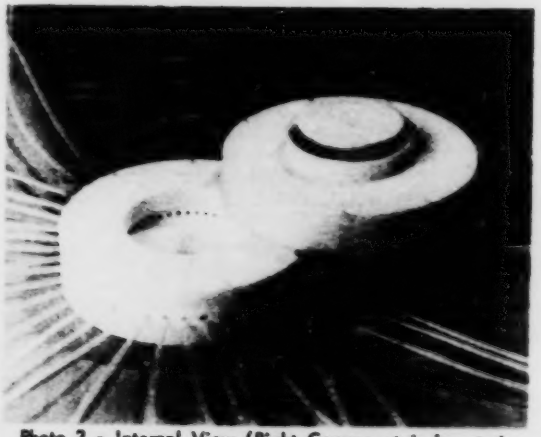
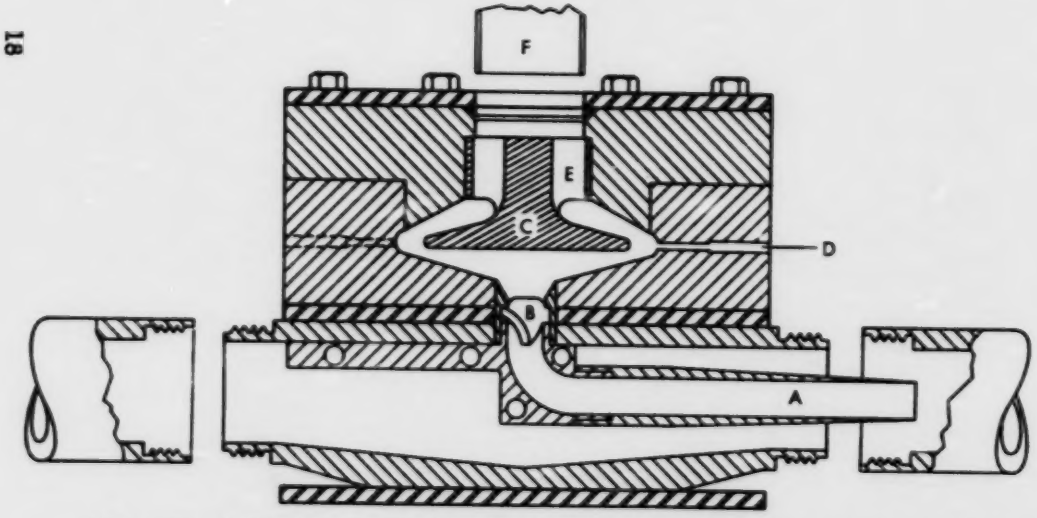


Photo 2 - Internal View (Right Component is Inverted in this Photo).



Cross section of all-TFE Teflon manifold with pickup tube (A), mixing impeller (B), main chamber flow spreader (C), exits to collaborator ports (D), channel to exhaust manifold (E), and manifold exhaust duct (F). Gas not captured by pickup assembly exhausts at left side of manifold base. Double cross-hatched assembly plates at top, middle, and bottom are stainless steel.

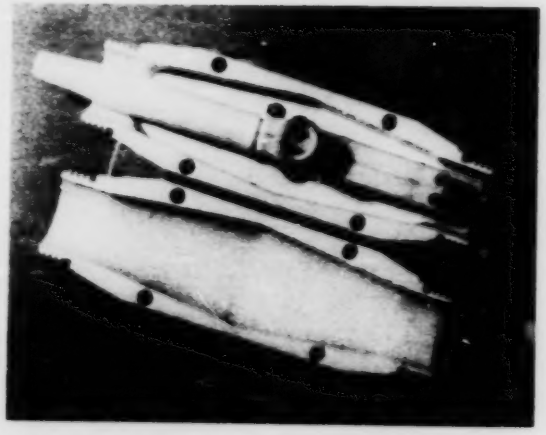


Photo 3 - Internal View of Manifold Pickup Section Showing Flow-Spiraling Impeller.

Figure 8. Schematic drawing and photographs of the sampling manifold

Section A of the manifold is in the pickup tube through which flows the total volume of gas sampled by the collaborators. The inlet to this pickup tube is located such that this volume is drawn from the central portion of the main stream. The sampled volume flows past a mixing impeller (B) and then into the main chamber of (C) of the manifold. In this chamber, the flow is spread evenly to the 45 symmetrically located exit channels (D). The gas in the main chamber that is not drawn through the exit channels to the collaborator ports flows out the exhaust duct or purge line which has a control valve. Both exhaust lines from the manifold join downstream to form a common exhaust tube, which also contains a flow control valve.

One port of each sampling manifold is used to monitor the pressure in the sampling manifold to determine if it remains positive (see schematic drawing of Figure 3). Another port of each manifold is used to monitor the NO_2 and NO levels being sampled by the collaborators. A Bendix Model 8101 B chemiluminescence NO-NO_2-NO_x analyzer is used for this and is switched between the spiked and unspiked manifolds. (See photograph 12 of Figure 3.)

SYSTEM CHECKOUT

Readying the system for the collaborative test comprised three principal areas of activity: (1) determination of levels of NO and NO_2, both ambient and inside the building; (2) checkout of the sampling system, including monitoring devices and test instrumentation; and (3) checkout of the sampling system as an operational system. These three areas are discussed below.

Ambient Levels of NO and NO_2

Ambient levels of nitrogen oxides at the test site were generally low, but there were considerable variations at these levels. Since the test site is located in a rural area south of Kansas City where there is very little industry, the primary factors that influence NO_x levels at the site are wind speed and wind direction.

During tests of NO_x levels using MRI's Bendix Model 8101 B chemiluminescence NO-NO_2-NO_x analyzer for 24-hr monitoring, the lowest levels were found when the wind was from the south. Both NO and NO_2 seldom exceeded 20 $\mu g/m^3$. Periods of more than 1-hr duration were measured when readings were indistinguishable from the purified zero gas used to calibrate the analyzer.

With northerly winds, NO_2 levels were generally between 30 and 50 $\mu g/m^3$ and NO levels were approximately 10 $\mu g/m^3$. As expected, the ambient levels followed an inverse relation with respect to wind speed. The highest daily readings were coincident with the morning and evening rush hours. These peak levels generally began at about 7:00 a.m. and again at 5:00 p.m. and lasted between 2 to 4 hr.

The highest recorded levels of NO occurred under calm wind conditions when the light vehicular traffic in the vicinity of the test station generated levels in excess of 100 $\mu g/m^3$. NO levels did not exceed NO_2 levels at this site.

Over a 24-hr period, average NO_2 levels were 10-50 $\mu g/m^3$, and NO levels were of the order 10-20 $\mu g/m^3$. During any 24-hr period, maximum NO_2 levels were generally several times higher than the minimum levels. Thus, while NO_2 levels at the test site are lower than those at urban, industrial locations, the NO_2 levels do exhibit the variability found under normal ambient conditions. Indoor readings were similar but did not show the sudden changes often found when monitoring outdoor levels.

Subsystems and Units

The venturi and dry-gas meter were calibrated using a 1.0 ft^3/min wet-test meter. Information concerning the calibration is given in Appendix C. The entire system was prepared for the test by bringing all components to normal operating conditions several days prior to the test and running the system continuously in this mode until the beginning of the test. Water addition to the constant-temperature bath was the only maintenance required. The temperature variation of the permeation-tube bath during this time was less than 0.1°C. A check of NO_x levels in the cylinders of prepurified nitrogen carrier gas found no NO_2 and 40 $\mu g/m^3$ NO.

The Bendix NO_x Analyzer was checked at MRI by a Bendix field representative. The difference in spiked and unspiked readings of the Bendix analyzer agreed within 10% of the calculated spike levels at all four levels used for the test. The instrument was stable and reliable when operated continuously at the levels found during normal testing. Checks with calibration gases reveal that the catalytic convertor efficiency does fall off sharply above 400 $\mu g/m^3$.

The symmetry of the sampling ports was checked in two ways. The primary way was that the pressure drop at each port was measured under the normal load of 200 cc/min. This test showed that all ports gave a pressure drop of 1.5 cm of water $\pm$ 0.5 cm. Such a pressure drop should have no effect on normal sample flows and the flowrate from the ports should be identical to that obtained by pulling free room air into the sampling trains.

A second way was to connect the NO_2 monitor to ports of the spiked and unspiked sampling manifolds and measure the level of NO_2 in micrograms per cubic meter. This was done in two ways: the system under a load, e.g., a spiked level of approximately 350 $\mu g/m^3$; and an unloaded condition where just ambient air was passed through each section--spiked and unspiked--of the NO_2 sampling system. In both cases, the NO_2 monitor showed no variation between four ports spaced equally around the manifold.

System Operation

Identical materials and dimensions are used on the spiked and unspiked sections of the NO_2 sampling system. Handling and treatment of all components were also identical.

Flowrates of the spiked and unspiked sides were within 10% of each other with all dampers open. In normal operation, the exhaust dampers are adjusted to give a positive pressure of 2-4 mm water at the sample manifolds. Once set, this pressure is stable.

The rise and fall times to equilibrium in response to changes in a spike level were checked. Rise time was less than 15 min and fall time was less than 5 min (when permeation tubes were disconnected). The fall time is essentially that of the analyzer response time, allowing for the purge time of the sample lines. The rise time is longer than the fall time because of the increased pressure against which the carrier gas stream must work when a set of permeation tubes are connected. Some flow reversal in the permeation-tube holders occurs after connection.

Since the response times were essentially limited by flowrates and instrument response, no observable adsorption effects were noted. Checks of NO_x levels found at the sampling ports agreed, within normal accuracy limits, with those measured outside the building. At the 50 $\mu g/m^3$ level both readings were within 5 $\mu g/m^3$ (0.5% of full scale), which is within the accuracy of the monitoring instrument. Thus, the unspiked samples at the sample ports accurately reflect ambient levels and the sampling system may be considered to be inert with respect to NO_2.

TEST SITE

The general criteria one would use in selecting a site include the ambient level of NO_2 and variation thereof, general meteorological and climatological conditions, work facilities for the collaborators (adequate space, facilities, housing, etc.), cooperation of the organization furnishing the site, logistic aspects, and local lodging accommodations.

The levels of NO_2 required are those representative of ambient NO_2 conditions, which are in the range of a few micrograms per cubic meter to 350 $\mu g/m^3$. These levels could be achieved at one site with a low level of NO_2 by spiking the ambient air with various levels of NO_2 in a manifold sampling system.

MRI's field station (see Figure 9) which is located in a rural area south of Kansas City, meets all the criteria and was selected as the test site. The NO_2, ambient-air sampling station is housed in building 3 shown in Figure 9. The input to the sampling system is located outside the building near the roadway (see photograph 3 of Figure 3).

The test facilities are described in conjunction with the sampling system (see pages 7-19). Photographs of the facilities are given in Figure 10. Photograph 1 shows the circular tables that house the sampling manifolds and the collaborators' sampling trains. Each table--spiked and unspiked--has a multiplicity of AC power receptacles, with each collaborator having its own branch of outlets. Each branch has its own circuit breaker and branch indicator (see photograph 2 of Figure 10). This arrangement is to protect other collaborators in case one collaborator has a power failure due to faulty equipment.

Photograph 3 of Figure 10 gives a close-up view of some of the collaborators' trains positioned in their table areas (see Figure 11). Photograph 4 of Figure 10 gives a view of part of the bulletin board where test instructions and general information was posted.

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DERAMUS FIELD STATION

Figure 9. Collaborative test site: MRI's field station

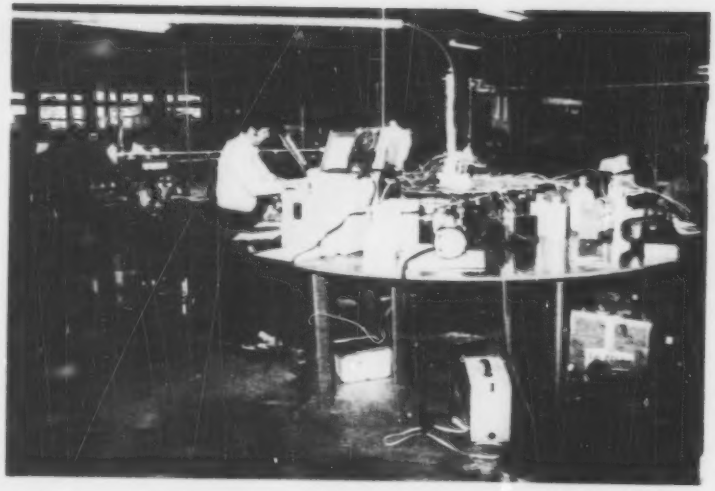


Photo 1 - Unspiked Table in the Forefront; Spiked Table in the Rear.

Photo 2 - AC Power Control and Visual Indicator; the Boarded Windows to Keep Out EM Radiation.

Photo 3 - Collaborators' Sampling Trains on Spiked Table; Spiked Sampling Manifold on Shelf above Table.

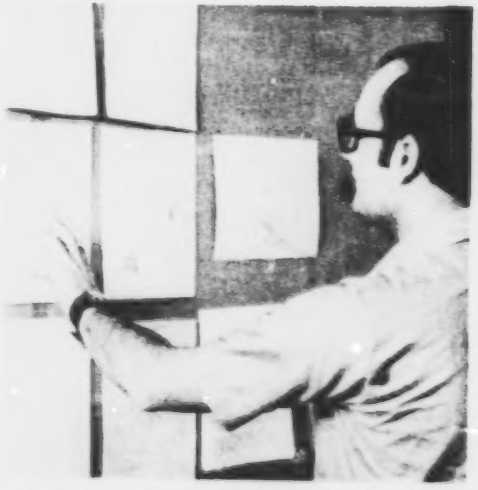
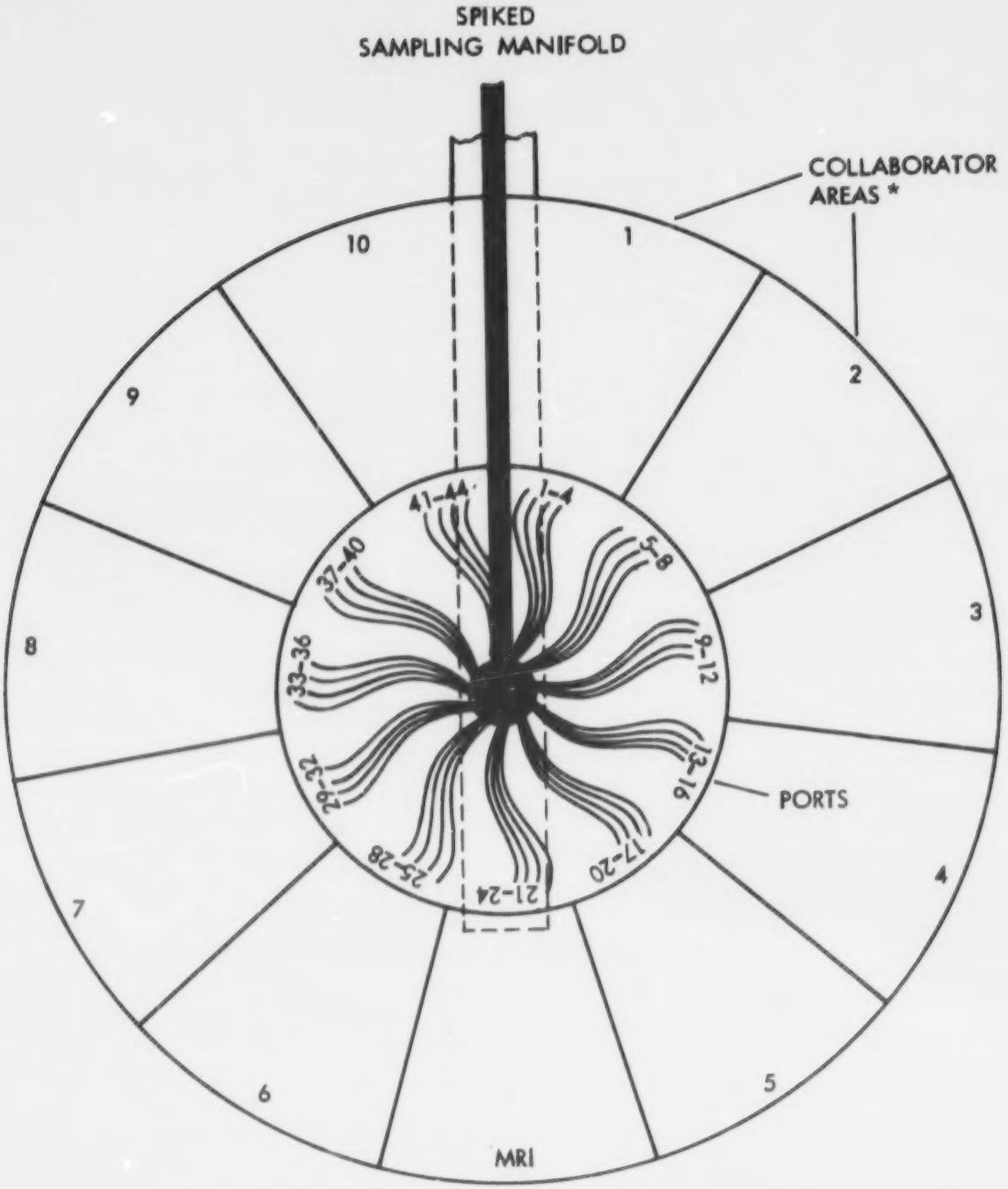


Photo 4 - Collaborators' Bulletin Board with Test Requirements, Gereral Information, etc.

Figure 10. Photographs of the test facility



* For unspiked manifold--collaborator areas marked in reverse order--counter clockwise.

Figure 11. Collaborators' sampling areas at the test site

Photographs 1, 2, and 3 of Figure 10 show that the windows on the north side of the building were boarded to keep electromagnetic radiation from entering the building. With this blockage and a temperature control system in the building, the 25.1°C permeation bath was able to be maintained at that temperature throughout the four 24-hr runs with no detectable deviation from the 25.1°C temperature, except for a few hours when the deviation was 0.1°C.

SELECTION OF COLLABORATORS

A principal activity was to compile a list of potential collaborators and from this list select 10 to perform the testing according to the tentative TGS-ANSA method. Information was obtained from EPA (names and addresses of 150 organizations) and from MRI's files to compile a list of nearly 200 potential collaborators.

A letter was sent to 162 organizations seeking their desire to participate as a volunteer collaborator on this test and evaluation program. Attached to this letter was a "Collaborator Form" to be completed which surveyed their experience with the four methods, methods they had used, equipment they could make available for the tests, acceptable length of test period, etc. A second letter was sent to those who expressed interest in the TGS-ANSA method after a test date was selected. A copy of these letters and the collaborator form are given in Appendix D.

A majority of the responses indicated the desire that a test period for a method be no more than 6 days.

Ten organizations were selected for the TGS-ANSA collaborative test from those organizations that responded in the affirmative to participate in the test. The selection was based upon the following criteria:

1. Willingness to participate on a volunteer basis,

2. Technical capabilities,

3. Related past experience,

4. Availability,

5. Ability to furnish sampling equipment, instruments, and materials required to perform the test strictly according to the method, and

6. Type of organization (industrial, educational, governmental--local, state, federal--etc.).

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The information needed to make the selection based on the above criteria was obtained from the collaborator forms that were returned, and from subsequent telephone conversations with the candidate collaborators.

The 10 organizations selected as collaborators for the TGS-ANSA collaborative test were:

Kentucky Division of Air Pollution
311 East Main Street
Frankfort, Kentucky 40601
502-564-3382
(Ms. Diana Dunker, Mr. Joe Andrews[1,2/])

Shell Development Company
P.O. Box 481
Houston, Texas 77001
713-667-5661
(Mr. J. H. Bradley, Mr. W. T. Shebs[1,2/])

City of Philadelphia Air Management Services Laboratory
1501 East Lycoming Street
Philadelphia, Pennsylvania 19124
215-288-5117
(Mr. Donald Kutys[1,2/])

North Ohio Valley Air Authority
814 Adams Street
Steubenville, Ohio 43952
614-282-3098
(Mr. Frank G. Norris, Mr. Dan Zorbini[1,2/])

State of New York
Department of Health
Division of Laboratories and Research
New Schotland Avenue
Albany, New York 12201
518-457-3118
(Ms. Barbara Kladatos[1,2/])

1/ These individuals performed the sampling at the field site.
2/ These individuals performed the analyses of the samples.

Kennecott Copper Corporation
Utah Copper Division
P.O. Box 11299
Salt Lake City, Utah 84111
810-322-1533
(Dr. Robert J. Heaney, Mr. Lynn A. Hutchinson[1,2/])

San Bernardino County Air Pollution Control District
172 West Third Street
San Bernardino, California 92415
714-383-1661
(Mr. Mark Villalabbos, Dr. C. Kenneth Wilcox[1,2/])

Mecklenburg County Department of Public Health
1200 Blythe Boulevard
Charlotte, North Carolina 28203
704-374-2607
(Mr. James T. Ward[1,2/])

Air and Industrial Hygiene Laboratory
State of California Health and Welfare Agency
Department of Health
2151 Berkeley Way
Berkeley, California 94704
415-843-7900
(Mr. Emil R. de Vera, Mr. Kenneth Smith[1,2/])

National Bureau of Standards
B 326 Chemis ry Building
Washington, D.C. 20234
301-921-2886
(Dr. John K. Taylor, Mr. Bob Deardorff[1,2/])

These organizations will be referred to as Collaborators A through J, without defining which is A, B, etc., to allow the organization data to remain anonymous.

STATISTICAL DESIGN

GENERAL CONSIDERATIONS AND COMMENTS

The purpose of this collaborative test was to determine the precision and bias of the TGS-ANSA method. A major element of the collaborative test was to have an experimental design that would allow this purpose to be met. Considerations that formed the bases of this design, which is given later in this section in a formal manner, are:

1. Challenge (spike) levels of NO_2,
2. Ambient levels of NO_2,
3. True values of NO_2,
4. Sampling time of a run,
5. Test period of the method,
6. Number of collaborators,
7. Number of samples per run,
8. Interferences,
9. Adsorptivity,
10. Sampling ports, and
11. Instrumentation.

Challenge (spike) level of NO_2 is an experimental design variate. Four levels of challenge were selected based upon the normal range of values found in ambient air on a 24-hr average basis: one low level on the order of 50 $\mu g/m^3$; two medium levels, one near 100 $\mu g/m^3$ and the second near 200 $\mu g/m^3$; and one high level of approximately 300 $\mu g/m^3$.

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A challenge level should be steady state, or continuous at a specific level, plus or minus acceptable deviations--less than $\pm$ 2%.

Ambient levels should be lower than the lowest challenge (spike) level (~ 50 $\mu g/m^3$). Since the ambient levels are the actual ambient levels of NO_2 at the test site, those levels present during the time of testing may vary from this criteria (see pages 19 and 20). The ambient levels will be mixed with the challenge levels to provide the spiked challenges. There will be just ambient challenges which are identical with the ambient portion of the spiked challenges. The collaborators will sample both spiked and ambient challenges simultaneously.

For a run, the true value of NO_2 sampled by the collaborators will be taken as the NO_2 spiked level generated by the permeation tube assembly plus the average value of the ambient challenges sampled by the 10 collaborators. The error involved here adds to the overall error in the analysis.

The TGS-ANSA method requires a sampling period to be 24 hr.

From the survey for volunteer collaborators, it was determined that 6 days would be the limit for a test period of a method. Thus considering this period, the mandatory 24-hr sampling period (or a run) travel time, and orientation, set-up and switch-over time (time in between runs), four runs would be the maximum possible.

Ten collaborators were deemed to be sufficient to obtain a cross-section of the population of the type organizations that would be involved in sampling NO_2, be within acceptable project costs, and provide statistical significance with the results.

Replicate samples are desirable and generally needed. In this test, replication is constrained by the test period and the duration of a run, and thus any replicates must be of the nature of simultaneous sampling by collaborators using as near identical trains as possible. This type replication, in turn, has constraints, which include principally the number of collaborators, space limitations at the test site, size of the NO_2 sampling system and cost limitations. Naturally some of these are interdependent.

An important consideration for the TGS-ANSA method is that of interferences. These factors will vary depending upon geographic location, time of year, etc. The interference consideration was not included in the experimental design, since work had shown that the method did not have any known interferences.*

* See Section 3 of Appendix A.

Adsorptivity is of concern because of the possibility of error in the NO_2 level received by the collaborators' sampling devices in contrast to the known level of the challenge--from both the standpoints of increasing and decreasing the challenge level from run to run. Teflon material was used from the NO_2 bleed-in port through the sampling manifold to minimize if not eliminate the adsorptivity factor. For further assurance, prior to commencing a run, the challenge could be run for a sufficiently long period so that all surfaces exposed would have reached a state of equilibrium with the new concentration. Both aspects were covered; Teflon was used in the construction and sufficiently long challenges were made to the system prior to commencing a run.

The port-to-port effect did not need to be incorporated in the experimental design because results of the evaluation of the NO_2, ambient-air sampling system indicated that all ports were identical (see first paragraph of page 21).

The major considerations with regard to instrumentation for the TGS-ANSA collaborative test were: (1) MRI would only instruct the collaborators that they are to use the sampling equipment and calibration specified in the method writeup, and (2) MRI's monitoring instrumentation and test instrumentation used in the calculation of the NO_2, ambient-air system was sufficiently reliable and accurate. In both cases, all requirements were met.

THE FORMAL DESIGN

The NO_2 data are collected according to a two-way analysis of variance model with the analysis of primary interest being estimation of the components of variance and the bias. Thus, the mean square errors can be constructed.

Specifically, we have:

$$X_{ijk} = \mu + C_i + L_j + CL_{ij} + e_{k(ij)}$$

where
μ = overall mean,
C_i = i^{th} collaborator ($i = 1, \ldots 10$; C_i is a random factor),
L_j = j^{th} level of NO_2 ($j = 1, \ldots 4$; L_j is a fixed factor),
CL_{ij} = collaborator-level interaction,
$e_{k(ij)}$ = error term ($k = 1, \ldots, 4 \; \forall \; ij$),*
X_{ijk} = k^{th} response observed by i^{th} collaborator on j^{th} level.

* $\forall$ means "for every."

The expected mean squares are:

$$E(MS_C) = \sigma_e^2 + 16\,\sigma_C^2,\quad E(MS_L) = \sigma_e^2 + 4\,\sigma_{CL}^2 + 40^{*}\,\sigma_L^2,\quad E(MS_{CL}) = \sigma_e^2 + 4\,\sigma_{CL}^2$$

and

$$E(MS_e) = \sigma_e^2$$

Although the F-tests for significant effects were performed for completeness, the primary object is the components of variance analysis; in particular, the components σ_e^2 (variance of repeated observations) and σ_c^2 (variance between collaborator means).

Let

N_{js} = spiked level j of NO_2,
N_{ijk} = k^{th} observation by i^{th} collaborator at level j of NO_2,
$\bar{A}_{\cdot j}$ = average of collaborators' observations of ambient NO_2 at level j,

then

$$X_{ijk} = ijk^{th} \text{ response} = (N_{ijk} - \bar{A}_{\cdot j}) - N_{js}.$$

Therefore, X_{ijk} is the ijk^{th} deviation from the true (bias) subject only to the error in using $\bar{A}_{\cdot j}$ as the true ambient level. It would, of course, be desirable to have no error at all in the true values, but the above method of estimating bias is preferable to no estimate at all. Thus, we produced mean square error (per collaborator, if necessary) estimates in addition to variance estimates.

In any analysis of variance the homeoscedastic assumption must be validated. It was found that the measurement error was relatively uniform throughout the experiment, i.e., not a function of the level of NO_2. Therefore, no data transformation was made (see page 46 for detailed discussion).

Outliers were deleted before analysis, and the frequency of them noted. One collaborator produced useless results (see Appendix H). Therefore, the results are reported using nine collaborators.

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* Collaborator I was deleted from the actual analysis (see page 41), so $E(MS_L) = \sigma_e^2 + 4\,\sigma_{CL}^2 + 36_L^2$.

COLLABORATORS' FIELD SAMPLING

The collaborative test took place at the MRI Deramus Field Station during 29 April - 3 May 1974. The 10 collaborators (see Figure 12), started the test at 0830, 29 April, with an orientation. The NO_2, ambient-air sampling system they used was shown and explained to them. The written instructions that comprise Appendix D were given to and discussed with the collaborators. After this orientation period the collaborators set up their sampling trains in preparation for the first run. They were ready to start sampling at 11:20 a.m., 2 hr ahead of schedule. The actual schedule of the four runs that took place is given in Table 1. All 10 collaborators cleared the site by 1500, Friday afternoon, 3 May.

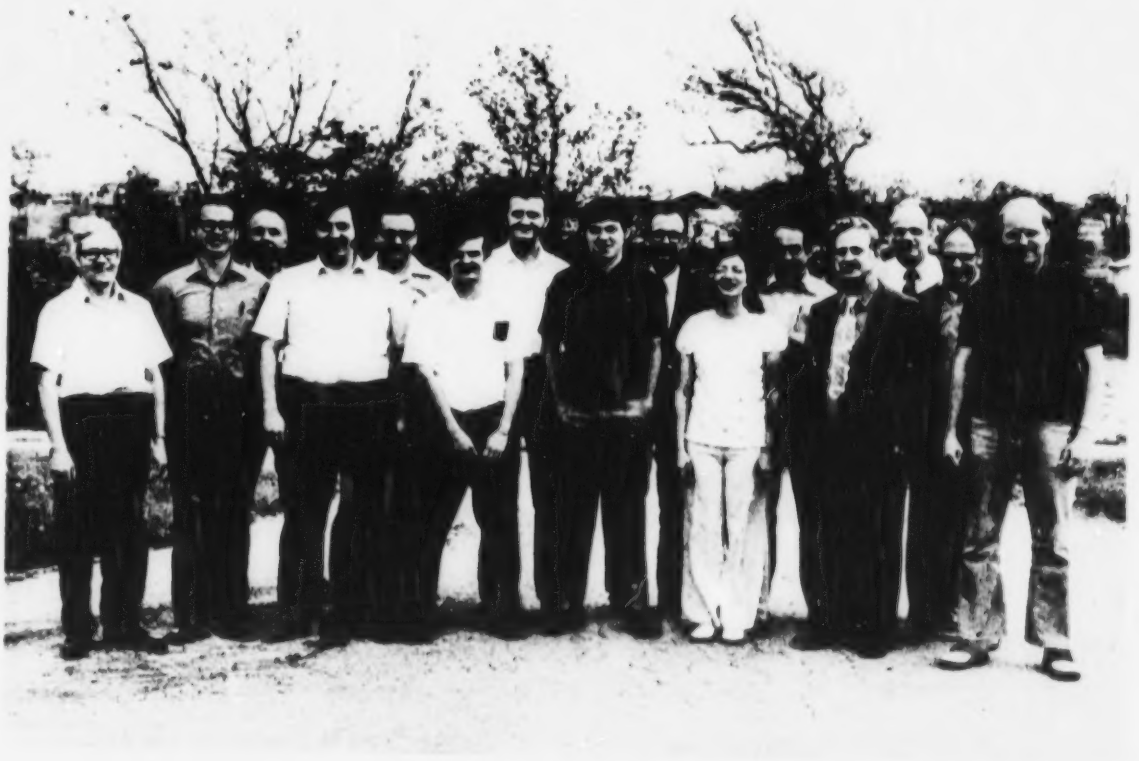
Table 1. TGS-ANSA COLLABORATIVE TEST SCHEDULE

Run	NO Spiked Level (g/m)	Date/Time Started	Date/Time Completed
1	65.6	4-29-74 at 1120	4-30-74 at 1120
2	117	4-30-74 at 1207	5-1-74 at 1207
3	223	5-1-74 at 1239	5-2-74 at 1239
4	315	5-2-74 at 1304	5-3-74 at 1304

Each run was 24 hr in duration. The collaborators were at the site from 2 to 3 hr prior to the start of the run, or completion of a run. They stayed through the change over to the subsequent run and from 1 to 2 hr thereafter.

During the test MRI personnel observed that all collaborators followed the sampling procedures given in the method writeup, and their equipment met the requirements presented therein.

The collaborators prepared their absorbing solutions at their home laboratories, to minimize biasing.



Front Row: Bob Deardorff, Lynn Hutinson, Don Zorbini, Kenneth Wilcox, James Ward, Barbara Kladatos, Paul Constant 1/, Donald Kutys

Back Row: Bob Stuttz 1/, George Scheil 1/, Kenneth Smith, Fred Bergman 1/, Joe Andrews, John Margeson 2/, W.T. Shebs

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1/ MRI personnel.
2/ EPA Project Monitor.

Figure 12. Photograph of field personnel of the NO_2 collaborative test (TGS-ANSA Method); MRI field station; 29 April - 3 May 1974

Field data were recorded in duplicate by the collaborators on data sheets designed by MRI for this test (see Figure 13). A copy of this data sheet was collected from each collaborator after the completion of a run, and before a subsequent run would be started. The collaborators retained their copies for recording subsequent analysis work at their home laboratories.

During 23-25 April--just prior to the start of the test on Monday, 29 April--MRI prepared standard samples. These samples were drawn from the spiked line (first day) and unspiked line (second day) into absorbing solutions which were contained in 200-ml impingers. The solutions from all impingers were mixed for each day to provide a homogeneous sample. Individual samples were then prepared for the collaborators and MRI. Each collaborator was given two NO_2 sample and one blank (absorbing solution only) to be analyzed at his home laboratory along with his test samples. MRI followed the method in preparing for sampling and sampling with the exception that the trains were scaled upward.

The samples taken by the collaborators, as well as MRI's standard samples given to them, were either taken with them when they returned home, or shipped to them by MRI. The samples were shipped via Air Mail on different days to insure against loss of all samples of a collaborator in case a shipment was lost or destroyed.

MRI had a laboratory supervisor who was in charge of the NO_2, ambient-air system operation. He was on duty from 0800 to 1700 each day, which was the period of run starts and completions. He was available anytime during the 24-hr runs, if any problems arose, as was the program manager.

There was a technician on duty throughout each run at all times during the test. These people monitored the sampling system operation, recording operational data and general observations. A general log book was kept as well as the log sheet for operational data. Copies of these log sheets are given in Appendix F.

MRI DERAMUS FIELD STATION - K.C. MO.

NITROGEN DIOXIDE DATA SHEET - SODIUM ARSENITE METHOD

Sampling

Collaborator _____ Run Number _____
Sampled by _____ Sampling Port Number _____

Sampling Train No. _____

Bubbler Identification No. _____

Rotameter Description (make, model, etc.,) _____
_____

Rotameter reading at start _____ at finish _____ type of ball _____

Start: Date _____ Time _____ Finish: Date _____ Time _____

Sampling duration (min) _____ Sample flow rate (cm^3/min) _____

Total air volume sampled (m^3) _____

Remarks:

Analysis

Date of Analysis _____

Analyzed by: Person _____ Organization _____

Standardization plot slope (absorbance units/μg NO_2/ml)_____

Absorbance of sample against blank (540 nm) _____ Aliquot (ml) _____

NO_2 Concentration (μg/m^3) _____

Remarks:

Figure 13. Nitrogen dioxide data sheets--TGS-ANSA method

ANALYSES OF SAMPLES

This section discusses the analyses performed by the collaborators and by MRI. The collaborators' analyses were of the samples they took during the test from both the spiked and unspiked lines, and the standard samples prepared by MRI and given to them. For each of the four test runs in the field, each collaborator had four spiked samples and two unspiked samples. In addition, each collaborator had three standard samples--one blank and two NO_2. System operational data logged by MRI during the four tests are given in Appendix F.

ANALYSES PERFORMED BY THE COLLABORATORS

The collaborators performed the analyses of their samples according to the procedures given in the TGS-ANSA method, with one exception: Collaborator I reported an extremely low slope for his calibration curve and his results were low by approximately a factor of 10. Further information was then obtained which revealed that the error was apparently caused by contaminated methanol, which was in violation of the method specifications. The collaborator reported that the dye did not dissolve and had to be filtered before use. Previous use of this methanol had not exhibited this behavior. A sample of the methanol was subsequently sent to MRI. The liquid was clear and colorless with a small amount of white gelatinous precipitate. The methanol was in a fresh 5-gal. metal can, not used for other purposes. Apparently ANSA prepared before the collaborative test was taken from the relatively uncontaminated top portion of the can, while the methanol used later was from the more contaminated bottom of the can.

In all cases, the collaborators' representative who performed the field sampling also performed the analyses of the samples at the collaborators' home laboratory. The collaborators' comments on the test are given in Appendix G.

Table 4. COLLABORATIVE RESULTS FROM COLLABORATIVE TEST USING THE [illegible] METHOD

		A	MRI	B	MRI	C	MRI	D	MRI	E	MRI	F	MRI	G	MRI	H	MRI	I[1]	MRI	J	MRI
Run 1																					
Spike = 94 µg/m³	Spiked	102.40	105	127	127.0	115	112	127.3	127	116.0	116	108.5	109	116.1	115	[illegible]	106	[illegible]	[illegible]	103.5	108
		110.86	113	110	112.2	108	106	119.5	120	117.4	117	109.9	111	116.1	118	55.98[2]	55	10.72	11.5	111.7	112
		107.10	108	99	101.4	80[2]	76	122.5	122	127.4	128	115.9	117	117.8	117	102.17	109	9.68	9.0	107.5	106
		106.67	105	128	134.1	120	118	123.9	124	114.8	115	85.1	86	122.6	121	59.56[2]	58	8.90	8.6	113.6	114
	Unspiked	16.18	19.1	28	27.1	29	28.3	27.5	27.5	25.3	25.3	26.1	26.1	29.9	29.6	17.42	16.8	3.90	4.2	22.3	22.2
		16.91	19.8	25	24.7	32	28.8	27.8	27.8	25.2	25.2	27.6	27.7	43.1	42.6	17.73	17.3	3.23	3.5	29.8	29.7
Run 2																					
Spike = 197 µg/m³	Spiked	225.95	229	189	190	197	195	236.3	235	211.0	213	145.9	147	218.8	217	234.30	230	[illegible]	24.2	213.5	212
		224.89	229	196	196	203	200	225.5	226	218.4	218	146.8	148	216.9	216	227.10	224	21	22.5	183.1	183
		209.18	211	201	202	188	184	227.0	227	219.0	219	145.7	144	223.2	223	231.34	228	5.47	7.0	207.9	206
		212.75	216	192	190	207	203	230.9	231	216.2	216	175.3	176	220.8	219	234.71	231	19.41	20.8	213.6	213
	Unspiked	19.65	22.3	26	25.2	23	24.6	27.7	27.8	25.2	25.2	26.5	26.7	27.5	27.2	22.74	22.7	1.92	2.1	30.2	29.7
		20.31	23.6	24	23.5	30	25.6	27.7	27.7	26.2	26.7	26.1	26.2	29.1	28.8	17.33	16.9	2.15	2.3	30.5	29.7
Run 3																					
Spike = 54.1 µg/m³	Spiked	70.42	70	28[2]	27.3	73	69	67.2	67	60.6	61	61.1	61	57.3	57	44.55	43.5	16.67	15.5	58.6	62
		63.17	67	50	48.1	62	58	66.3	66	61.0	61	59.0	59	59.4	59	50.99	49.9	13.97	15.0	67.0	65
		59.85	62	58	57	55	60	64.4	64	63.2	63	58.3	59	50.8	60	40.28	39.6	3.23	3.5	66.0	65
		57.31	60	58	56	65	60	66.2	66	60.2	60	56.0	56	59.4	59	44.09	43.1	4.31	10.4	64.8	64
	Unspiked	5.84	9.0	12	11.8	15	10.5	14.1	14.1	13.0	13.0	13.2	13.1	14.0	13.8	4.71	4.8	1.01	1.0	16.7	16.9
		5.11	7.2	16	14.7	21	13.9	14.6	14.7	14.3	14.3	13.5	13.6	12.5	12.4	4.71	4.9	5.39	6.1	19.1	19.9
Run 4																					
Spike = 302 µg/m³	Spiked	307.69	308	252	254	288	286	330.7	331	313.8	316	276.7	276	298.4	296	301.34	294	31.71	35.6	295.2	294
		327.52	328	211[2]	211	225[2]	21.6	327.7	328	316.4	316	270.3	272	298.8	296	296.43	290	34.80	41.8	305.6	305
		298.30	298	272	274	295	293	325.2	323	315.1	315	288.1	291	300.6	304	307.43	301	47.5	50.9	292.9	292
		301.99	302	288	285	291	288	327.3	328	312.5	313	267.4	269	305.4	301	307.87	300	41.09	45.2	291.8	290
	Unspiked	9.82	10.9	17	16.3	15	10.6	12.6	12.6	11.9	11.9	15.7	17.9	14.1	13.4	6.06	5.8	.90	9.4	18.6	19.3
		9.73	10.3	17	16.2	17	12.7	13.2	13.2	12.9	12.9	16.5	16.4	13.1	14.9	6.12	5.9	2.27	2.4	18.6	19.1
Standards (µg/ml)																					
(MRI's values = 0.004)		0.025		0.05		0.05		0.067		0.068		0.073		0.048		0.034		0.018		0.36	
= 0.64		0.645		0.55		0.66		0.672		0.643		0.63		0.546		0.684		0.511		0.73	
= Blank		0		0.02		0		0.015		0.018		0.032				0		0.016		0.02	

1/ All Collaborator I results deleted from subsequent analyses.
2/ These points deleted as outliers in subsequent analyses.

COLLABORATORS' RESULTS

The one primary set of results the collaborators furnished MRI is the results of their chemical analysis of their samples. These data, which include calibration and absorbance data relating to these results, as well as raw field data that resulted from sampling in the field, are given in volume 2 of this report.

For convenience, these final results of the collaborators analyses are summarized in Table 2. There are two sections to Table 2: the top portion that gives measurements from the test samples taken by the collaborators; and the bottom portion that gives the results of the collaborators' analyses of the standard samples given them. Column 1 of the top portion of Table 2 gives the NO_2 level that is mixed with the ambient air to form the run's challenge. It does not include the quantity of NO_2 that was present in the ambient air (see page 46 for information on the "True Value"). Column 2 and succeeding even columns provide the NO_2 values the collaborators measured during each run. There are six values per run; two are from the two samples taken from the ambient air (unspiked) manifold; and four are from the four samples taken from the spiked manifold (each collaborator pulled all six of his 24-hr samples simultaneously). Column 5 and succeeding odd columns provide the values MRI obtained when it checked the collaborators' calculations.

MRI's check of the collaborators' results was a gross overall check to determine if there were major errors due to, for example, misplacement of the decimal point. Minor difference could be attributed to the reading of the collaborators' calibration curves.

STATISTICAL ANALYSIS OF COLLABORATORS' RESULTS

Our analysis of variance model for the whole experiment is:

$$X_{ijk} = \mu + C_i + L_j + CL_{ij} + e_{k(ij)} \quad ,$$

where
- μ = overall mean,
- C_i = i^{th} collaborator, $i = 1, \ldots, 9$,[1/]
- L_j = j^{th} NO_2 level, $j = 1, \ldots, 4$,
- CL_{ij} = collaborator-level interaction,
- $e_{k(ij)}$ = residual error in k^{th} measurement in the ij^{th} cell, $k = 1, \ldots, 4$ $\forall$ ij, and
- X_{ijk} = ijk^{th} bias, i.e., ijk^{th} determination - true value.

The NO_2 level is a fixed factor, but the collaborators are considered to be a random factor; i.e., the nine collaborators used in the experiment are considered a sample drawn from a population of possible collaborators. Thus, the expected mean squares (EMS) are:

Term	EMS
C	$\sigma_e^2 + 16\ \sigma_c^2$
L	$\sigma_e^2 + 4\ \sigma_{CL}^2 + 36\ \sigma_L^2$
CL	$\sigma_e^2 + 4\ \sigma_{CL}^2$
e	σ_e^2

1/ Ten collaborators participated in the test, but one produced useless results (see discussion, page 41). See Appendix H for a statistical analysis including all 10 collaborators.

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The true value is the spiked level of NO_2 plus the ambient NO_2 the ambient level, of course, being unknown. Therefore, a true value is taken as the spiked amount plus the average ambient determination of all collaborators. For example, the true level one NO_2 is taken as 116.9 $\mu g/m^3$ because 94.1 $\mu g/m^3$ were spiked and the average ambient reading from the nine collaborators was 22.8 $\mu g/m^3$.

An individual response is a bias (collaborators' reading of the spiked line minus the true value). For example, collaborator A's first reading of the spiked line at level one was 102.4 $\mu g/m^3$, so X_{111} = 102.4 - 116.9 = -14.5 $\mu g/m^3$, etc. Since subtracting a constant is merely coding the data, the components of variance are unaffected by the use of biases rather than spiked readings as the response.

Six observations (out of 144) were discarded as outliers (via the Dixon test, $\alpha = 0.05$). The outliers were not associated with particular collaborators or particular NO_2 levels. All the outliers were, however, too low. The presence of six artificial observations means that the error degrees of freedom are 102 (rather than 108).

The assumption of homeoscedasticity was checked by computing the cell ranges (R_i) and $\bar{R}$ for each NO_2 level (see Table 3). The statistic $\bar{R}$ is proportional to σ, so that if $\bar{R}$ is related in some monotonic fashion to the NO_2 level (L), a data transformation would be indicated. Although $\bar{R}$ is not uniform, it is not a monotonic function of L, either, and the ratio $\bar{R}/L$ is less stable than $\bar{R}$ itself. In general, if $\bar{R}$ (i.e., σ) is not independent of L, a data transformation is indicated. In practice, however, one must find some reasonably simple relationship between $\bar{R}$ and L that is "more constant" than the original $\bar{R}$ itself. For instance, $\bar{R}/L$ or $(\bar{R}/L)^{1/2}$ or $(\bar{R}/L)^2$ or log $(\bar{R}/L)$ or $(\bar{R}/\log L)$ or $(\log \bar{R}/\log L)$, etc., should be more stable than $\bar{R}$ (without reference to L) in order for a data transformation to be indicated. For the NO_2 data in this test, such functions are no more stable than $\bar{R}$ itself, which is not surprising since $\bar{R}$ is essentially constant for the top three NO_2 levels. Therefore, no data transformation was applied. However, σ_e at the lowest NO_2 level is probably less than σ_e elsewhere, and the σ_e estimates per level were computed.

Table 3. $\bar{R}$ VERSUS NO_2 LEVEL

$\bar{R}$	L ($\mu g/m^3$)	$\bar{R}/L$ (%)
9.3	65.6 (L3)	14.3
13.2	116.9 (L1)	11.3
15.8	222.6 (L2)	7.1
15.5	314.7 (L4)	4.9

A complete analysis of variance was performed (see Table 4). The discussion of biases will be presented, and the components of variance analysis and discussion will follow.

Table 4. ANALYSIS OF VARIANCE (RESPONSE = BIAS)

Source	df	SS	MS	F
C	8	10,439.11	1,304.89	23.34
L	3	3,100.45	1,033.48	2.83
CL	24	8,760.67	365.03	6.53
e	102	5,702.18	55.90	-

BIASES

Collaborators differ significantly in their average bias, and the calibration curves (bias versus level) for the various collaborators are significantly nonparallel. However, bias depends slightly, if at all, on the NO_2 level ($F(3,24) = 2.83$, $0.10 < \alpha < 0.05$).

In general, collaborators read -9.5 $\mu g/m^3$ too low, i.e., about 5% below the true value (see Tables 4 and 5). The collaborators can be divided into four groups (via the Fischer method): two collaborators reading 21-23 $\mu g/m^3$ too low, three collaborators reading 11-13 $\mu g/m^3$ too low, three collaborators reading 2-6 $\mu g/m^3$ too low, and one collaborator reading 6 $\mu g/m^3$ too high. One collaborator exhibits no bias, i.e., produces an average reading not statistically different from zero.

Table 5. AVERAGE BIAS ($\mu g/m^3$) PER NO_2 LEVEL

NO_2 ($\mu g/m^3$)	Average Bias	Percent true
65.6	-6.4	-10
116.9	-3.9	-3
222.6	-12.0	-5
314.7	-15.7	-5
Overall average 180.0	-9.5	-5

Table 6. COLLABORATOR BIASES ($\mu g/m^3$) (ALL NO_2 LEVELS)

Collaborator	Average bias	Percent true	Group[a/]
A	-5.6	-3	C
B	-20.9	-12	A
C	-12.9	-7	B
D	6.4	4	D
E	-2.2	-1	C[b/]
F	-22.5	-13	A
G	-5.7	-3	C
H	-11.0	-6	B
J	-11.2	-6	B

a/ Members of a group do not differ significantly in (average) bias.
b/ - Not statistically different from zero.

Although, the CL interactions term is significant, almost all of the reason for the significance is due to two collaborators (see Table 7 and Figure 14). Collaborators H and G showed a much larger negative bias at the 66 $\mu g/m^3$ NO_2 level than they had at the other NO_2 levels. All other collaborators exhibited a relatively uniform percentage error for all NO_2 levels. Thus, in general, a calibration curve is relatively linear over the range of NO_2 examined.

Table 7. COLLABORATOR PERCENT BIAS PER NO_2 LEVEL

Collaborator	Percent Bias			
	65.6 $\mu g/m^3$	116.9 $\mu g/m^3$	222.6 $\mu g/m^3$	314.7 $\mu g/m^3$
A	-2	-9	-2	-2
B	-16	-1	-13	-14
C	-3	-2	-11	-7
D	0	+5	+3	+4
E	-7	+2	-3	0
F	-11	-10	-14	-12
G	-15	+1	-1	-4
H	-31	-10	0	-4
J	-2	-6	-8	-6

PRECISION

The components of variance σ_e^2 (dispersion of repeated measurements within a collaborator) and σ_c^2 (dispersion between collaborator averages) are shown in Table 8.

Table 8. COMPONENTS OF VARIANCE (ALL NO_2 LEVELS)

	Absolute standard error ($\mu g/m^3$)	Relative standard error (% true)
σ_e	7.48	4.2
σ_c	8.84	4.9
$\sqrt{\sigma_e^2 + \sigma_c^2}$	11.58	6.4

The two errors σ_e and σ_c are approximately the same size. On the average, a collaborator will read between $\pm$ 2 σ_e of his average "most" ($\sim$ 95%) of the time; a set of collaborators will read between $\pm$ 2 $\sqrt{\sigma_e^2 + \sigma_c^2}$ of their average most of the time, etc.

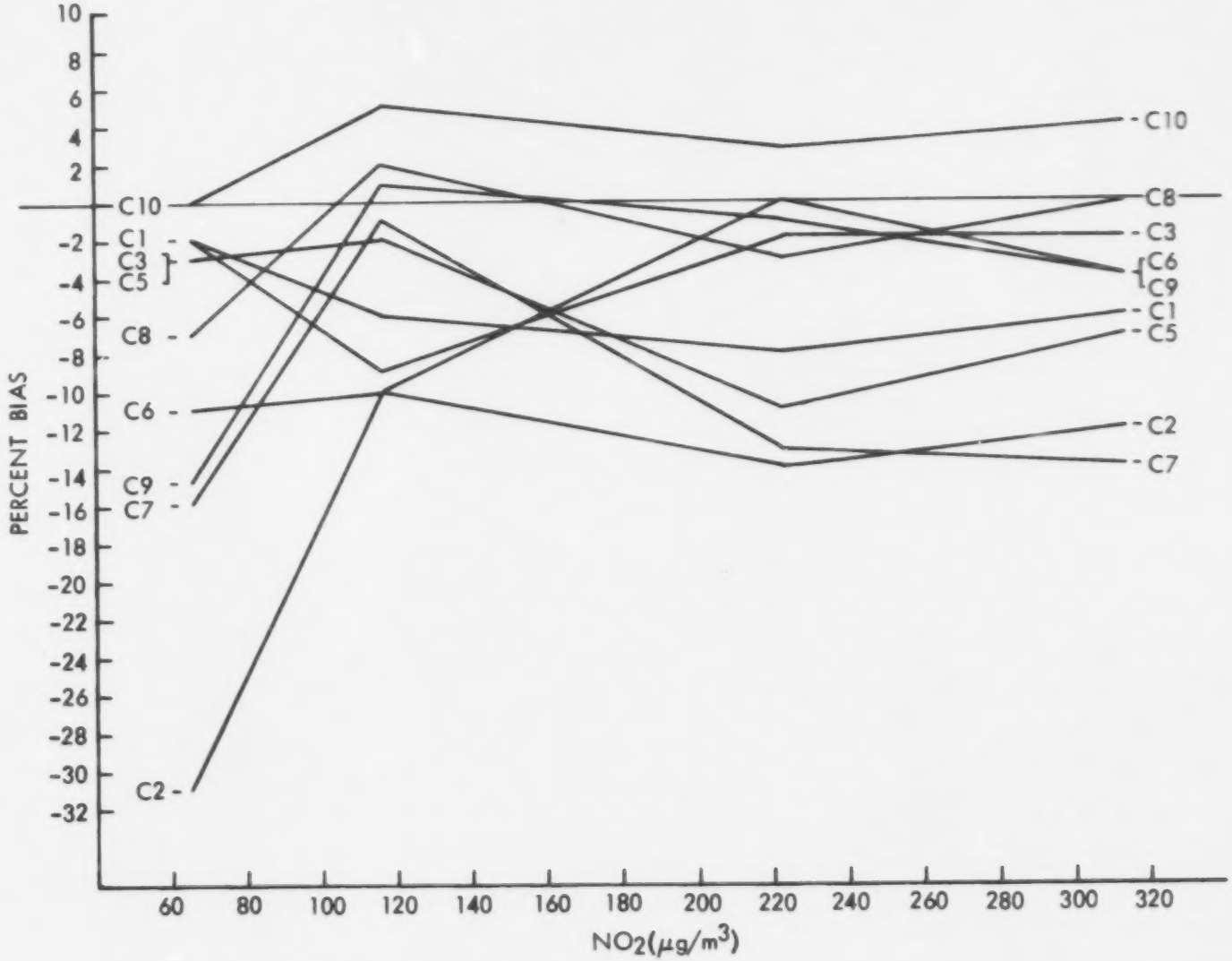

Figure 14. Collaborator percent bias versus level of NO_2

SUMMARY AND DISCUSSION OF STATISTICAL ANALYSIS

1. There is a general negative bias to the NO_2 measurements, but it is relatively small (approximately 5%) and nearly independent of the NO_2 level. Various collaborators differ in the amount of bias shown but this variability is also relatively small ($\sigma_c \sim 5\%$ true value).

2. The measurement errors are essentially uniform for all collaborators. Also, σ_e is constant for the three higher NO_2 levels, but somewhat smaller at the lowest NO_2 level. In general, σ_e is about 4% of the true value, but is about 7% of the true value at the lowest NO_2 level.

3. Although two collaborators exhibited nonlinear calibration curves due to much larger biases at the lowest NO_2 level than elsewhere, in general the calibration curves are relatively linear.

4. Two points regarding the usefulness of the estimates should be mentioned:

a. A replicate in this experiment is not a genuine replicate, since all duplicate readings were taken simultaneously. Physically, the fact that the collaborators did not have to "gear up" to produce a replicate probably depresses the σ_e estimates. Mathematically, the measurement errors are perhaps dependent, i.e., correlated due to the way the test was performed. The effect of such dependence on the σ_e estimates can be in either direction; a positive correlation inflates σ_e and vice versa.

b. The higher the NO_2 level, the more reliable the relative bias estimate, since the unknown ambient becomes an increasingly smaller fraction of the NO_2 amount.

LOWER DETECTABLE LIMIT (LDL)

Two meanings of LDL are used in the following discussion: (a) the smallest value of NO_2 that can be reliably identified as existing (i.e., positive) when the method is used by a collaborator (a "pure" LDL) and (b) the smallest reliable value of NO_2 determined by a set of collaborators using the method (a "practical" LDL).

Three methods of estimating the LDL were used. The first method is based upon the set of blank readings, and falls, more or less, into the category of a rule of thumb. The average blank value was doubled to estimate the LDL; this results in a value of 2 $\mu g/m^3$.

The second method of estimating the LDL used the ambient readings of the collaborators obtained during the actual experiment. Using the within-collaborator standard deviation (σ_e) of 1.86 $\mu g/m^3$, an estimated "pure" LDL of about 3.7 $\mu g/m^3$ is calculated. Incorporating the collaborator-collaborator standard deviation (σ_c = 4.69 $\mu g/m^3$, $\sqrt{\sigma_e^2 + \sigma_c^2}$ = 5.05 $\mu g/m^3$), an estimated "practical" LDL of about 10 $\mu g/m^3$ is obtained. Note that there is no way of incorporating the bias into these estimates, since the true ambient levels are not known.

The third method of estimating the LDL used the collaborators' calibration curves* themselves by computing the standard errors of the estimate (s.e.'s) of the calibration lines. To estimate the pure LDL, the average s.e. was doubled; to estimate the practical LDL, the s.e. from all collaborators combined was doubled. This yields a pure LDL estimate of 4 $\mu g/m^3$, and a practical LDL estimate of 10 $\mu g/m^3$. Note that in this data set a bias estimate is possible, and in fact the intercept of the combined calibration curve is + 4.6 $\mu g/m^3$ (rather than zero). Thus, the pure LDL is about 9 $\mu g/m^3$, and the practical LDL is 15 $\mu g/m^3$, when the bias is accounted for.

The three sets of results seem to agree well. It seems reasonable to state that the pure LDL is probably $\leq$ 9 $\mu g/m^3$, and the practical LDL $\leq$ 15 $\mu g/m^3$.

---

* The only available calibration curves were from collaborators C, E, F, and G.

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CONCLUSIONS

The major conclusions that can be drawn from the results of this collaborative test are:

1. The NO_2, ambient-air sampling system developed by MRI is an effective system for use in collaborative testing of manual methods such as the TGS-ANSA procedure.

2. The "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA Procedure)" is adequately written for those knowledgeable of sampling and analysis techniques as presented therein.

3. If the tentative TGS-ANSA procedure as given in Appendix A of this report is followed by people knowledgeable of the sampling and analysis techniques given therein, then such persons will obtain results with an average bias of -9.5 $\mu g/m^3$ over the range 50-300 $\mu g/m^3$. The precisions can be estimated from the within laboratory standard deviation (σ_e) of 7.5 $\mu g/m^3$, and the collaborator standard deviation (σ_c) of 8.8 $\mu g/m^3$.

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RECOMMENDATIONS

Based upon the conclusions that have been drawn from the results of this collaborative test, it is recommended that:

1. The same NO_2 sampling system be used in the evaluation of the remaining NO_2 methods to be tested;

2. The data sets to be obtained from the subsequent methods to be evaluated be based on experimental designs, test procedures and sampling system operational procedures as similar as possible to those of the TGS-ANSA collaborative test so that comparisons of the methods are based on similar criteria; and

3. No further analysis be made of the results from the TGS-ANSA method until the results from the other three methods are obtained.

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APPENDIX A

TENTATIVE METHOD FOR THE DETERMINATION OF NITROGEN DIOXIDE IN THE ATMOSPHERE (TGS-ANSA PROCEDURE)

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ENVIRONMENTAL PROTECTION AGENCY

METHODS STANDARDIZATION BRANCH

QUALITY ASSURANCE AND ENVIRONMENTAL MONITORING LABORATORY

NATIONAL ENVIRONMENTAL RESEARCH CENTER

RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

APRIL 1974

TENTATIVE METHOD FOR THE DETERMINATION OF NITROGEN DIOXIDE IN THE ATMOSPHERE (TGS-ANSA)[a]

[a]A tentative method is one which has been carefully drafted from available experimental information, reviewed editorially within the Methods Standardization Branch and has undergone extensive laboratory evaluation. The method is still under investigation and therefore is subject to revision.

1. Principle and Applicability

1.1 Nitrogen dioxide is collected by bubbling air through a solution of triethanolamine, o-methoxyphenol and sodium metabisulfite.[1] The nitrite ion produced during sampling is determined colormetrically by reacting the exposed absorbing reagent with sulfanilamide and 8-anilino-1-naphthalenesulfonic acid, ammonium salt.

1.2 The method is applicable to collections of 24-hour samples in the field and subsequent analysis in the laboratory.

2. Range and Sensitivity

2.1 The range of the analysis is 0.025 to 4.0 µg NO_2^-/ml. Beer's law is obeyed throughout this range. With 50 ml of absorbing reagent and a sampling rate of 200 cm^3/min for 24-hours, the range of the method is 20 to 700 $\mu g/m^3$ nitrogen dioxide.

2.2 A concentration of 0.025 µg NO_2^-/ml will produce an absorbance of approximately 0.025 using 1 cm cells.

3. Interferences

3.1 At a nitrogen dioxide concentration of 100 $\mu g/m^3$ the following pollutants, at the levels indicated, do not interfere: ammonia, 205 $\mu g/m^3$; carbon monoxide, 154,000 $\mu g/m^3$; formaldehyde, 750 $\mu g/m^3$; nitric oxide, 734 $\mu g/m^3$; phenol, 150 $\mu g/m^3$; ozone, 400 $\mu g/m^3$ and sulfur dioxide, 439 $\mu g/m^3$.

3.2 A temperature of 40°C during collection of sample had no effect on recovery.

4. Precision and Accuracy

4.1 Precision and Accuracy

4.1.1 On making measurements from standard nitrogen dioxide atmospheres, prepared by using permeation devices, a relative standard deviation of 2% and a collection efficiency of 93% were determined throughout the range of the method.

4.2 Stability

4.2.1 The absorbing reagent is stable for 3 weeks before sampling and the collected samples are stable for 3 weeks after sampling.

5. Apparatus

5.1 Sampling. A diagram of a suggested sampling apparatus is shown in Figure 1.

5.1.1 Probe. Teflon, polypropylene, or glass tube with a polypropylene or glass funnel at the end.

5.1.2 Absorption tube. Polypropylene tubes 164 x 32 mm. equipped with polypropylene two-port closures. Rubber stoppers cause high and varying blank values and should not be used. A glass tube restricted orifice is used to disperse the gas. The tube, approximately 8 mm O.D.-6 mm. I.D., should be 152 mm long with the end drawn out to 0.3-0.6 mm. I.D. The tube should be positioned so as to allow a clearance of 6 mm from the bottom of the absorber.

5.1.3 Moisture trap. Polypropylene tube equipped with a two port closure. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with glass wool to prevent moisture entrainment.

5.1.4 Membrane Filter, 0.8-2.0 microns porosity.

5.1.5 Flow Control Device. Any device capable of maintaining a constant flow through the sampling solution between 180-220 cm^3/min. A typical flow control device is a 27 gauge hypodermic needle,[2] three-eights inch long. (Most 27 gauge needles will give flow rates in this range.) The device used should be protected from particulate matter. A membrane filter is suggested. Change filter after collecting 10 samples.

5.1.6 Air Pump. Capable of maintaining a pressure differential of at least 0.6-0.7 of an atmosphere across the flow control device. This value includes the minimum useful differential, 0.53[(2)] atmospheres, plus a safety factor to allow for variations in atmospheric pressure.

5.1.7 Calibration Equipment. Flowmeter for measuring airflows up to 275 cm^3/min. within ± 2%, stopwatch, and a precision wet test meter (1 liter/revolution).

5.2 Analysis

5.2.1 Volumetric Flasks. Two each 250, 1000 ml; three each 200; 7 each 100 ml; one 500 ml.

5.2.2 Pipets, volumetric. One each, 2, 3, 9, 10, 20 and 50 ml; seven 5

5.2.3 Pipets serological, graduated in 1/10 ml divisions. One each 1, 5 ml.

5.2.4 Test Tubes. Each approximately 20 x 150 mm.

5.2.5 Spectrophotometer. Capable of measuring absorbance at 550 nm.

5.2.6 Graduated cylinder. One each 50 ml.

6. Reagents

6.1 Sampling

6.1.1 Triethanolamine [$N(C_2H_4OH)_3$]. Reagent grade.

6.1.2 o-Methoxyphenol (o-$CH_3OC_6H_4OH$). Also known by its trivial name, guaiacol. Reagent grade. Melting point 27-28°C. (Caution: Technical grade material will not meet this specification and should not be used).

6.1.3 Sodium Metabisulfite ($Na_2S_2O_5$). ACS reagent grade.

6.1.4 Absorbing Reagent - Dissolve 20g of triethanolamine, 0.5g of o-methoxyphenol, and 0.250g of sodium metabisulfite consecutively in 500 ml of distilled water. Dilute to one liter with distilled water. Mix thoroughly. The solution should be colorless. This solution is stable for three weeks if protected from light.

6.2 Analysis

6.2.1 Hydrogen Peroxide (H_2O_2). ACS reagent grade, 30%.

6.2.2 Sulfanilamide [4-$(H_2N)C_6H_4SO_2NH_2$]. Melting point 165-167°C.

6.2.3 8-Anilino-1-naphthalenesulfonic acid Ammonium salt (ANSA) (8-C_6H_5NH-1-$C_{10}H_6SO_3^-NH_4^+$). Minimum analysis, 98%.

6.2.4 Sodium Nitrite, [$NaNO_2$]. ACS reagent grade. Assay of 97% $NaNO_2$ or greater.

6.2.5 Methanol, absolute [CH_3OH]. ACS reagent grade.

6.2.6 Hydrochloric acid, [HCl]. Concentrated. ACS reagent grade.

6.2.7 Hydrogen Peroxide Solution. Dilute 0.2 ml of 30% hydrogen peroxide to 250 ml with distilled water. This solution can be used for a month if protected from light and refrigerated.

6.2.8 Sulfanilamide Solution (2.0% in 4N HCl). Dissolve 2.0g of sulfanilamide in 33 ml of concentrated HCl and dilute to 100 ml with distilled water. Mix. This solution can be used for two weeks, if refrigerated.

6.2.9 AMSA Solution. (0.1% W/v). Dissolve 0.1g AMSA in 50 ml absolute methanol. Dilute to 100 ml with absolute methanol in a volumetric flask. Mix. Keep stoppered, when not in use, to minimize evaporative losses. Prepare fresh daily. (CAUTION: Older reagent may result in lower absorbance).

6.2.10 Standard Nitrite Solution. Dissolve sufficient desiccated sodium nitrite and dilute with distilled water to 1000 ml so a solution containing 1000 μgNO_2^-/ml is obtained. The amount of $NaNO_2$ to use is calculated as follows:

$$G = \frac{1.500}{A} \times 100$$

where

G = Amount of $NaNO_2$, grams.

1.500 = Gravimetric factor in converting NO_2 into $NaNO_2$

A = Assay, percent

7. Procedures

7.1 Sampling. Assemble the sampling apparatus, as shown in Figure 1. Components upstream from the absorption tube may be connected, where required, with teflon or polypropylene tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with tygon, teflon or polypropylene. Add exactly 50 ml of absorbing reagent to the calibrated absorption tube

(8.1.3). Disconnect funnel, insert calibrated flowmeter (8.1.1) into the end of the probe and measure flow before sampling. Denote as F_1. If flow rate before sampling is not between 180-220 cm^3/min replace the flow controlling device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate in this range. Sample for 24-hours and measure the flow after sampling by again inserting a calibrated flowmeter into the probe, after removing the funnel. Denote as F_2.

7.2 Analysis. Replace any water lost by evaporation during sampling by adding distilled water up to the calibrated mark on the absorption tube. Mix well. Pipet 5 ml of the collected sample into a test tube, add 0.5 ml of the peroxide solution and mix vigorously for approximately 15 seconds. Add 2.7 ml of sulfanilamide solution and mix vigorously for about 30 seconds. Then pipet 3 ml of the ANSA solution, mix vigorously for about 30 seconds. The ANSA must be added within 6 minutes of mixing the sulfanilamide solution. (CAUTION: Longer time intervals will result in lowered absorbance values). Prepare a blank in the same manner using 5 ml of unexposed absorbing solution. The absorbance of the blank should be approximately the same as the y-intercept in the calibration curve (Section 8.2). Determine absorbance at 550 nm with distilled water in the reference cell using 1 cm cells. The color can be read anytime from 1 to 40 minutes after addition of the ANSA. Read $\mu g\ NO_2^-/l$ from the calibration curve (Section 8.2).

7.3 Spectrophotometer cells must be rinsed thoroughly with distilled water, acetone, and dried, otherwise a film will build up on the cell walls.

8. Calibration and Efficiencies

8.1 Sampling

8.1.1 Calibration of Flowmeter. (See Figure 2). Using a wet test meter and a stopwatch, determine the rates of air flow (cm^3/min) through the flowmeter at a minimum of four different ball positions. Plot ball position versus flow rate.

8.1.2 Flow Control Device. The flow control device results in a constant rate of air flow through the absorbing solution and is determined in 7.1.

8.1.3 Calibration of Absorption Tube. Calibrate the polypropylene absorption tube, (Section 5.1.2) by first pipeting in 50 ml of water or absorbing reagent. Scribe the level of the meniscus with a sharp object. go over the area with a felt-tip marking pen, and rub off the excess.

8.2 Calibration Curve. Dilute 5.0 ml of the 1000 µg NO_2^-/ml solution to 250 ml with absorbing reagent. This solution contains 20 µg NO_2^-/ml. Dilute 5.0 ml of the 20 µg NO_2^-/ml standard to 200 ml with absorbing reagent. This solution contains 0.50 µg NO_2^-/ml. Prepare calibration standards by pipeting the indicated volume of the standard into volumetric flasks and diluting to the mark with absorbing reagent.

Volume of Standard	Final Volume ml	Concentration µg NO_2^-/ml
10 ml of 0.50 µg NO_2^-/ml	100	0.05
20 ml of 0.50 µg NO_2^-/ml	100	0.10
2 ml of 20 µg NO_2^-/ml	200	0.20
Use 0.50 µg/ml Standard Directly	—	0.50
5 ml of 20 µg NO_2^-/ml Standard	100	1.00
5 ml of 20 µg NO_2^-/ml Standard	100	1.00

Run standards, plus a blank, as instructed in 7.2. Plot absorbance vs µg NO_2^-/ml. A straight line should be obtained with a slope of approximately 0.5 absorbance units/µg NO_2^-/ml, and a y-intercept (i.e., zero µg NO_2^-/ml) of approximately 0.01 absorbance units. The absorbance is linear up to a concentration of 4.0 µg NO_2^-/ml, absorbance of 1.9. Therefore, if samples exceed the absorbance of the highest calibration standard and the above absorbance is within the range of the spectrometer, the calibration curve can be extended by including higher concentration standards. If a higher absorbance range is not available, samples must be diluted with absorbing reagent until the absorbance is within the range of the highest standard.

8.3 Efficiencies. An overall average efficiency of 93% was obtained from test atmospheres having a nitrogen dioxide concentration of 20 to 760 µg/m^3.

9. Calculation

9.1 Sampling

9.1.1 Calculate volume of air sampled.

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-6}$$

V = Volume of air sampled m^3.

F_1 = Measured flow rate before sampling, cm^3/min.

F_2 = Measured flow rate after sampling, cm^3/min.

T = Time of sampling, min.

10^{-6} = Conversion of cm^3 to m^3.

9.1.2 Uncorrected Volume. The volume of air sampled is not corrected to S.T.P., because of the uncertainity associated with 24-hour average

temperature and pressure values.

9.2 Calculate the concentration of nitrogen dioxide as $\mu g\ NO_2/m^3$.

$$\mu g\ NO_2/m^3 = \frac{(\mu g\ NO_2^-/ml) \times 50}{V \times (0.93)}$$

50 = Volume of absorbing reagent used in sampling, ml.

V = Volume of air sampled, m^3.

0.93 = Overall efficiency of method.

9.2.1 If desired, concentration of nitrogen dioxide may be calcul as ppm NO_2.

$$ppm = (\mu g NO_2/m^3) \times 5.32 \times 10^{-4}$$

10. References

1. Saltzman, B. E., Suerst, R. G., Meeker, J. R., Guyer, M., Sawicki, E. "A Twenty-Four Hour Method for the Collection and Manual Colorimetric Analysis of Nitrogen Dioxide. Presented at the 165th ACS National Meeting in Dallas, Texas, April 8-13, 1973.

2. Lodge, J. P., Jr., Page, J. B., Ammons, B. E., Swanson, G. A. "The Use of Hypodermic Needles as Critical Orifices in Air Sampling." J.A.P.C.A. 16, 197-200 (1966).

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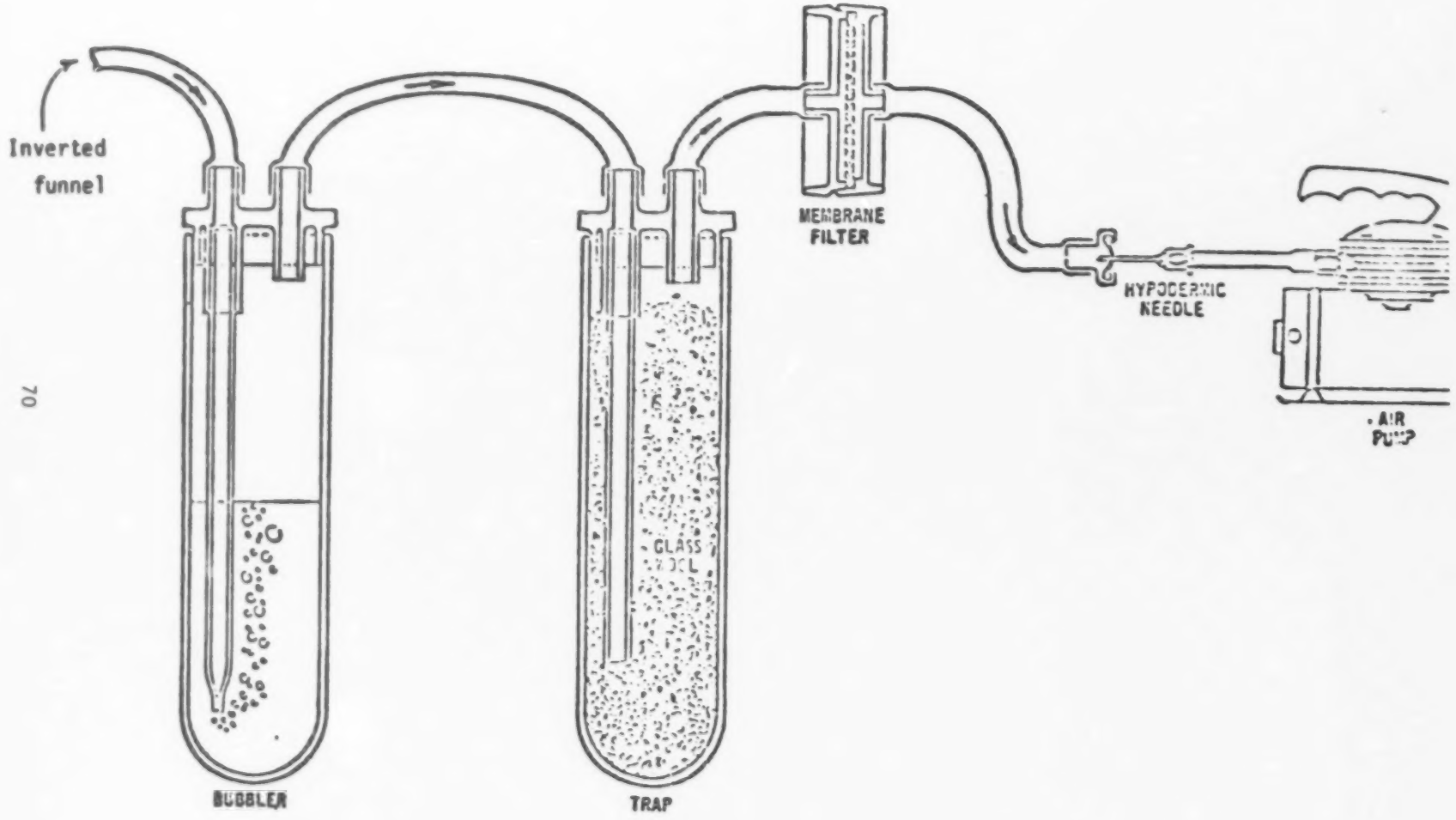

Figure 1. Sampling train.

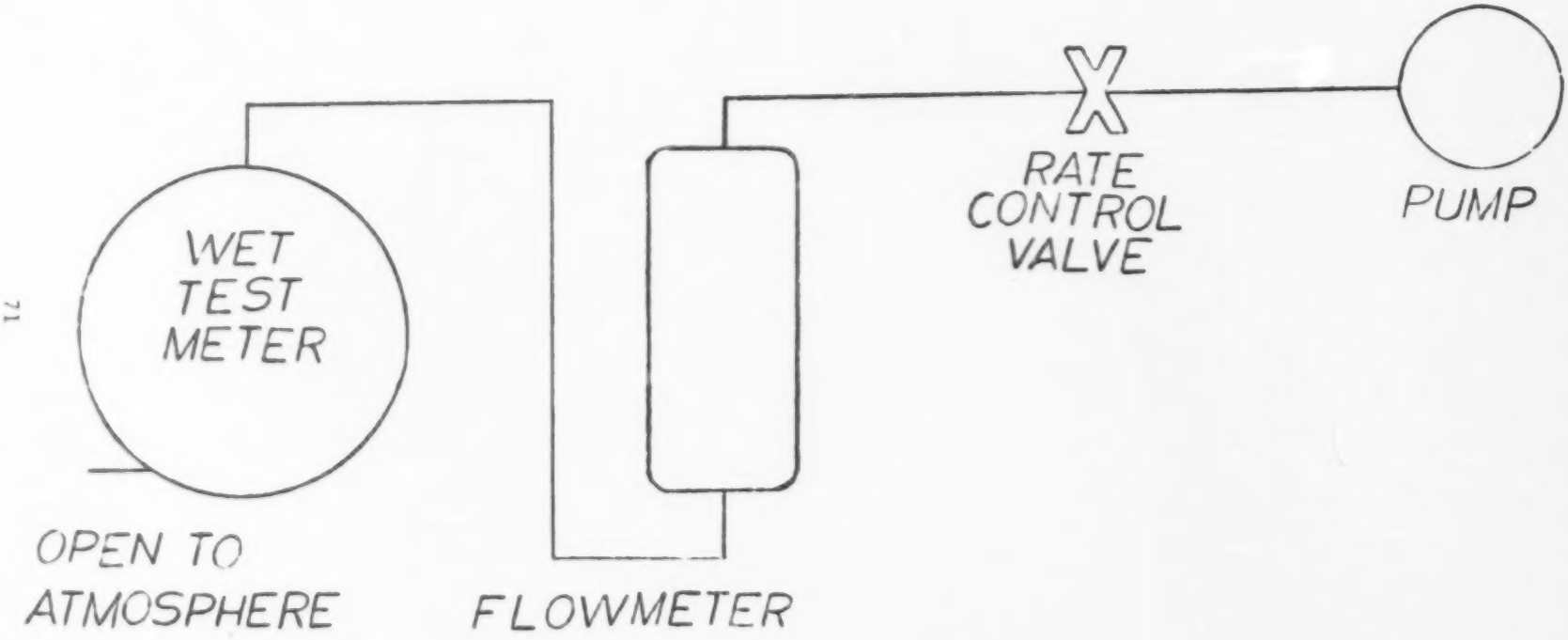
WET
TEST
METER
OPEN TO
ATMOSPHERE
FLOWMETER
RATE
CONTROL
VALVE
PUMP

FIGURE 2

APPENDIX B

DATA ON THE PERMEATION TUBES USED AS THE SOURCE OF THE SPIKED LEVELS OF NO_2

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As shown in Figure 6 of the text (p. 15), there were four branches to the NO_2 permeation tube assembly. Each branch contained a set of permeation tubes as follows:

Branch	Permeation Tube Number	Permeation Tube Rate of NO_2 (µg/min)	± 1 S (g/min)	Branch NO_2[a] (g/min)
4	29-2	1.210	0.001	-
4	34-12	1.770	0.002	-
4				2.980
3	35-13	1.990	0.003	-
3	29-4	1.210	0.001	-
3				3.200
1	35-8	1.434	0.001	-
1	35-16	1.597	0.002	-
1	29-3	1.345	0.002	-
1	28-10	1.160	0.002	-
1				5.536
2	34-3	1.195	0.002	-
2	34-13	1.275	0.002	-
2	34-6	1.548	0.001	-
2	34-1	1.226	0.003	-
2	34-10	1.138	0.001	-
2				6.382

[a] The sum of the NO_2 generated by each permeation tube in the branch.

Permeation rates for the above tubes were determined by the National Bureau of Standards and validated by the Methods Standardization Branch (MSB) of EPA at 25.1°C before they were given to MRI for use on the collaborative test.

The combinations of branches used for the four runs of the TGS-ANSA collaborative test are:

Run No.	Date	Branches Used
1	April 29-30	1
2	April 30 - May 1	1, 3 and 4
3	May 1-2	3
4	May 2-3	1, 2, 3 and 4

APPENDIX C

CALIBRATION OF THE VENTURI AND DRY-GAS METER

The venturi and dry-gas meter were calibrated using a 1.0-ft^3/rev, wet-test meter, as shown in Figure C-1. The wet-test meter is connected between the splitter and the dry-gas meter. A bubbler is used before the wet-test meter to saturate the air with water. The air flow then proceeds through the venturi to the NO_2 bleed-in as it does in normal operation.

Since the saturated air coming from the wet-test meter is not dried before going into the dry-gas meter, no correction for water vapor pressure is necessary and only the normal corrections for temperature and pressure are used. The flowrate of the wet-test meter (to stp) is:

$$Flow_{stp} = Flow_{(meter\ reading)} \times \frac{P}{760} \times \frac{294}{T}$$

where T = temperature of wet-test meter + 273, and
P = P_{atm} + pressure of test meter manometer.

The venturi flowrate is dependent on both temperature and pressure. Therefore $Flow_{stp}$ is corrected to venturi conditions.

$$Flow_{venturi} = Flow_{stp} \times \frac{760}{P_2} \times \frac{T_2}{294}$$

where T_2 = temperature of gas stream + 273, and
$P_2 = P_{atm} + P_{(gas\ stram)}$.

The dry-gas meter is temperature compensated, so only pressure corrections are made for its readings and a temperature base of 21°C is used for calibration. Thus the true flowrate of the dry-gas meter (F_m) is

$$F = Flow_{stp} \times \frac{760}{P_3}$$

where $P = P_{atm} + P_{(gas\ stream)}$.

The correction factor f to convert F_m, measured dry-gas meter flowrate, to true flowrate is then

$$f = \frac{F_m}{f_m}$$

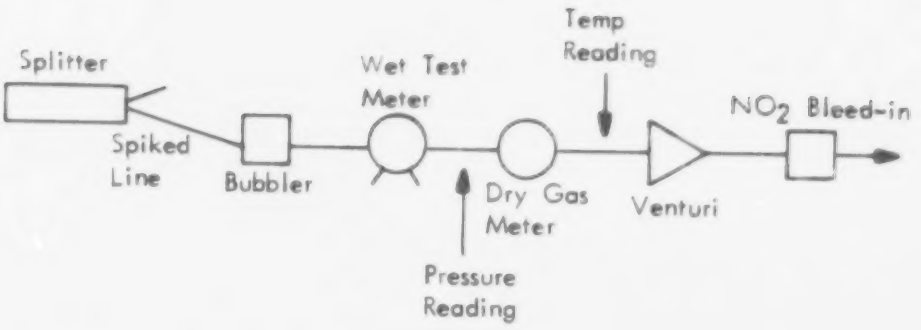

Figure C-1. Venturi and dry-gas meter calibration system

The venturi and dry-gas meter were calibrated at three flowrates; 50, 55, and 60 liters/min. Normal system flowrates are 55-60 liters/min. The calibration factor for the dry-gas meter is constant at the calibration flows ($\pm$ 0.2%). The average value of flow from seven determinations is used in calculating true flowrates of the system. The plot of venturi ΔP versus flowrate follows a straight line over the range used in calibration. From the slope and intercept of the line flowrates were calculated.

APPENDIX D

WRITTEN COMMUNICATIONS WITH POTENTIAL COLLABORATORS

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
Telephone (816) 561-0202

Dear Sir:

Your name has been given to Midwest Research Institute (MRI) by the Environmental Protection Agency (EPA), as having expressed an interest in becoming a voluntary collaborator in an NO_2 Testing Program, to be sponsored by EPA. I am writing to confirm this expression of interest by your organization.

The objective of this program is to determine the reliability and bias of four methods for measuring NO_2-ambient air. MRI has the responsibilities for organizing the program, furnishing the test facilities, coordinating the testing, analyzing the results of the collaborators, and reporting the findings to EPA.

The sodium-arsenite method--the first method to be evaluated--will be tested in Kansas City, Missouri, during the first part of January 1974. Ten collaborators are needed for each of the four methods. A tentative test schedule of the other three methods is given on the attached "Collaborator Form."

A writeup of the sodium-arsenite method is enclosed, and provides the information needed for a collaborator to perform the testing and analyze the samples he takes.

Each collaborator organization, once chosen, will be reimbursed for travel, subsistence, lodging, and miscellaneous expenses (e.g., shipment of equipment and local travel), for the employee sent to Kansas City to perform the testing. Each collaborator will need to furnish the sampling apparatus called for in the writeup. For each of the two manual methods, sodium-arsenite and TGS-ANSA, six sampling trains will be needed. Cases will be furnished in which to ship field samples to the collaborator's laboratory for analysis.

We would appreciate your completing and returning to us the Collaborator Form before November 15.

Sincerely,

Paul C. Constant, Jr., Head
Environmental Measurements Section

Enclosures: (1) Collaborator Form
(2) Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (Sodium-Arsenite Method)

COLLABORATOR FORM

1. Methods to Test (Check the ones in which you want to participate as a collaborator):

   ☐ Sodium Arsenite ☐ TGS-ANSA Procedure

   ☐ Continuous Saltzman ☐ Chemiluminescent

2. Equipment Available for Test:

   Could you furnish six trains for:

   Sodium Arsenite: ☐ yes ☐ no

   TGS-ANSA ☐ yes ☐ no

   Have you a Colorimetric (Continuous Saltzman) Ambient NO_2 Monitor?

   ☐ yes ☐ no Make _____ Model _____

   Have you a Chemiluminescent Ambient NO_2 Monitor that you would use?

   ☐ yes ☐ no Make _____ Model _____

3. Test Period (Each Method):

   Period acceptable (calendar days):

   ☐ 6 days ☐ 10 days ☐ 13 days

4. Methods You Have Used:

   ☐ Sodium Arsenite, ☐ TGS-ANSA, ☐ Continuous Saltzman,

   ☐ Chemiluminescent, ☐ Others: _____

   _____

   _____

5. Remarks: _____

   _____

   _____

   _____

   _____

6. Company: _____

   Address: _____

   Person to Contact: _____

   Telephone Number: _____

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
Telephone (816) 561-0202

21 February 1974

AIR MAIL

Name
Company
Address
City, State ZIP

Dear Mr. Name:

Last November you responded to a survey of ours indicating your interest in participating in an EPA-sponsored NO_2 Collaborative test using the TGS-ANSA Method. If you still desire to be considered as a candidate to participate in this test, would you:

1. Let me know before 8 March 1974;

2. Review the enclosed write up, "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA)," dated February 1974;

3. Use this TGS-ANSA technique exactly as presented to obtain five samples of NO_2 in the ambient atmosphere in your locality; and

4. Send me a copy of the results of your analysis of these five samples by 29 March 1974? (These results will be used to assist us in the selection of ten collaborators.)

The NO_2 collaborative test using the TGS-ANSA method is tentatively scheduled to take place in Kansas City, Missouri, starting the morning of 29 April and ending the afternoon of 3 May. The test will be indoors using a sampling system developed by MRI for this collaborative testing. (This system was used quite successfully for the sodium-arsenite method on a similar 5-day test in January.)

The sampling system that will be used in this test is shown in diagram form in Figure 1, an enclosure of this letter. Each collaborator will have four of his trains connected to the sampling manifold of the spiked line (bottom line of Figure 1) and two of his trains connected to the sampling manifold in the unspiked line. Thus, each collaborator is required to furnish a minimum of six of the trains that are specified in the enclosed write up.

The test schedule will require each collaborator to sample simultaneously at six ports of the sampling system during each of the four 24-hour runs that will constitute the 5-day test, to provide him 24 individual samples. In addition to these, he will be given several standard samples to analyze at his home laboratory along with the 24 collected. Wooden cases in which samples can be shipped to your home laboratory will be furnished on a loan basis.

As stated in our initial letter to your organization, each collaborator will be reimbursed for travel, subsistence, and lodging for the employee it sends to Kansas City to perform the field sampling, as well as local travel and miscellaneous expenses such as cost of shipping field equipment to be used on site for the sampling.

We will be in touch with you as soon as the ten collaborators are selected for this TGS-ANSA method. If you have any questions, please contact me.

Very truly yours,

Paul C. Constant, Jr., Head
Environmental Measurements Section

PCC:cdn

Enclosures:

1. "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA)"

2. Figure 1 -- NO_2 Ambient Air Sampling System

APPENDIX E

INSTRUCTIONS FOR COLLABORATORS NO_2 COLLABORATIVE TEST: METHOD TGS-ANSA PROCEDURE

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INSTRUCTIONS FOR COLLABORATORS

NO_2 COLLABORATIVE TEST: TGS-ANSA METHOD

GENERAL INFORMATION

1. Calibration, sampling, analysis, etc. should be done explicitly as stated in the April 1974 write-up furnished you on "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA)."

2. Each collaborator will have an area and a set of sampling ports at both the spiked-sampling-manifold table and at the unspiked table--see accompanying figure and table below:

Collaborator I.D.	Collaborator Name	Spiked Table Area	Spiked Table Ports	Unspiked Table Area	Unspiked Table Ports
1	Joe Andrews	1	1-4	1	41-44
2	W. (Bill) T. Shebs	2	5-8	2	37-40
3	Donald Kutys	3	10-13	3	33-36
4	Dan Zorbini	4	14-17	4	29-32
5	Ms. Barbara Kladatos	5	18-21	5	25-28
6	Lynn Hutchinson	6	25-28	6	17-20
7	Ken Wilcox	7	29-32	7	13-16
8	James Ward	8	33-36	8	9-12
9	Kenneth Smith	9	37-40	9	5-8
10	Bob Deardorff	10	41-44	10	1-4

3. For each run each collaborator will have six sampling trains running simultaneously: four in his area on the spiked table and two in his area on the unspiked table. Each train is to be attached to a separate port as specified in the above table.

4. Nitrogen Dioxide Data Sheets will be provided--a copy of one is attached. All information on sampling should be filled in during the period of the run. The bubbler identification number will be made by MRI's laboratory supervisor. He will have labels to affix to your samples. The coding is run number (1-4), followed by port number (1-45), followed by sampling table designation (S or U for spiked or unspiked), and terminated in collaborator number (1-10); e.g., 1-6-S-2 for run 1, port 6, spiked table

and collaborator 2 (W. T. Shebs of Shell Development Company). Analysis information is to be filled in at your home laboratory.

5. A copy of the data sheet for each run should be given to MRI's laboratory supervisor after each run is done.

6. Each collaborator should work independently of each other collaborator.

7. Shipping containers for the samples (absorbing tubes) will be available on a loan basis.

8. On the spiked sampling table, a separate power circuit (110-V, 60-cycle, four-outlet strip) is to be used by each collaborator for his four trains. On the unspiked line one strip will be shared by two collaborators. These strips are under the table tops near the periphery of the tops.

9. MRI will provide each collaborator with two standard samples (each of a different level of NO_2). This will raise the total number of samples to be analyzed by each collaborator to 26: six from each of four runs plus the two standard samples.

10. Each collaborator should analyze his samples at his home laboratory according to the tentative method write-up identified in Item 1 above. Results should be recorded on the Nitrogen Dioxide Data Sheets used in the field.

11. A copy of the completed data sheet on each sample as well as all calibration data and a complete description of the rotometer and wet-test meter used must be furnished MRI. All this information is needed by MRI within 1 month after completion of the field test.

TEST INSTRUCTIONS

1. Prepare your six sampling trains. Place four in your area on the spiked sampling table and two in your area on the unspiked sampling table.

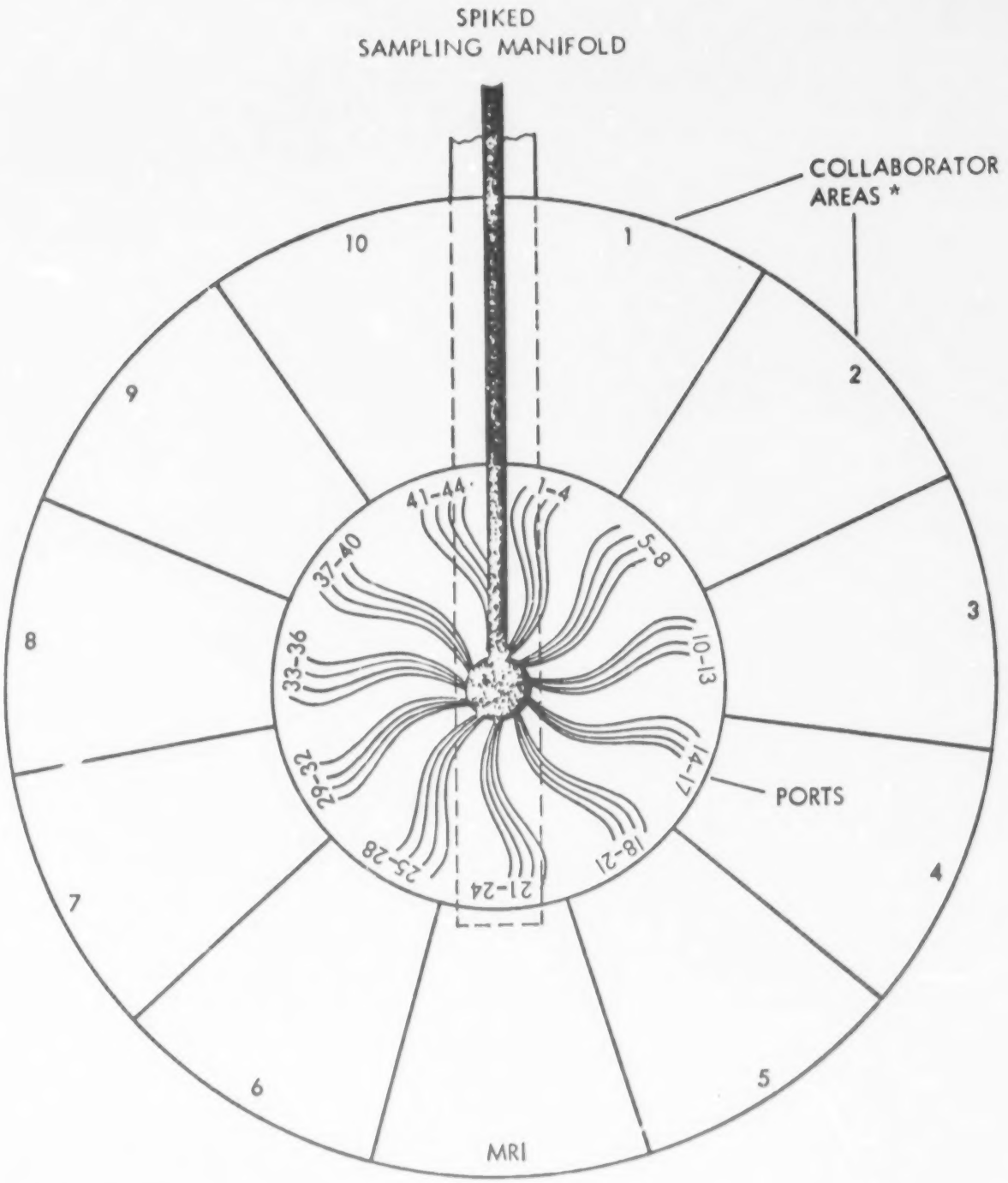
2. Prepare a data sheet for each sampling train.

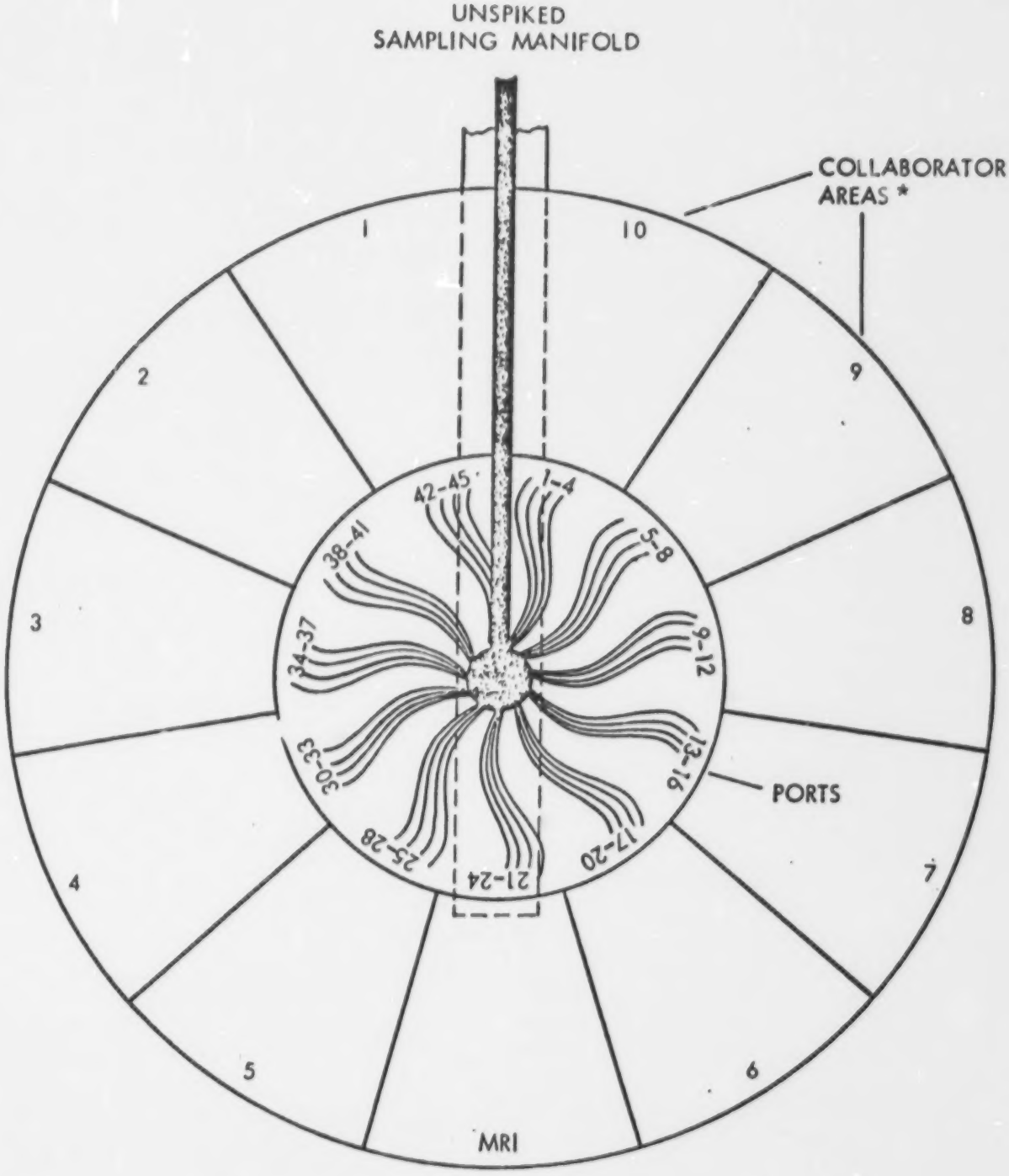
3. Upon notification of "Start testing," from the MRI laboratory supervisor, connect your trains to the proper ports and start your sampling according to the procedure in the April 1974 write-up on "Tentative

Method for Determination of Nitrogen Dioxide in the Atmosphere (TGS-ANSA)."

4. Upon notification, "Stop testing," from the MRI laboratory supervisor, terminate test according to the procedure in the method write-up.

NOTES


SPIKED
SAMPLING MANIFOLD
COLLABORATOR
AREAS *
1
2
3
4
5
6
7
8
9
10
MRI
PORTS
41-44
1-4
5-8
10-13
14-17
18-21
21-24
25-28
29-32
33-36
37-40


UNSPIKED
SAMPLING MANIFOLD
COLLABORATOR
AREAS *
1
2
3
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5
6
7
8
9
10
42-45
1-4
38-41
5-8
34-37
9-12
30-33
13-16
25-28
17-20
21-24
PORTS
MRI

COLLABORATORS

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Technical Services Program
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Ms. Barbara Kladatos
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Mr. Ken Wilcox
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Pollution Control District
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Mr. James T. Ward, Air Hygienist
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Environmental Health Division
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Mr. Kenneth Smith
Air and Industrial Hygiene Laboratory
State of California Health & Welfare
Agency
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2151 Berkeley Way
Berkeley California 94704
(415) 843-7900

Mr. Bob Deardorff
National Bureau of Standards
B 326 Chemistry Building
Washington, D.C. 20234
(301) 921-2886

MRI DERAMUS FIELD STATION - KANSAS CITY, MISSOURI

NITROGEN DIOXIDE DATA SHEET - TGS-ANSA METHOD

Sampling

Collaborator _____ Run Number _____
Sampled by _____ Sampling Port Number _____

Sampling Train No. _____

Bubbler Identification No. _____

Rotameter Description (make, model, etc.) _____

_____

Rotameter Reading At Start _____ At Finish _____ Type of Ball _____

Pump Vacuum At Start _____ At Finish _____

Start:Date _____ Time _____ Finish:Date _____ Time _____

Sampling Duration (min) _____ Sample Flow Rate (cm^3/min) _____

Total Air Volume Sampled (m^3) _____

Remarks:

Analysis

Date of Analysis _____
Analyzed by: Person _____ Organization _____

Standardization Plot Slope (absorbance units/μg NO_2/ml) _____

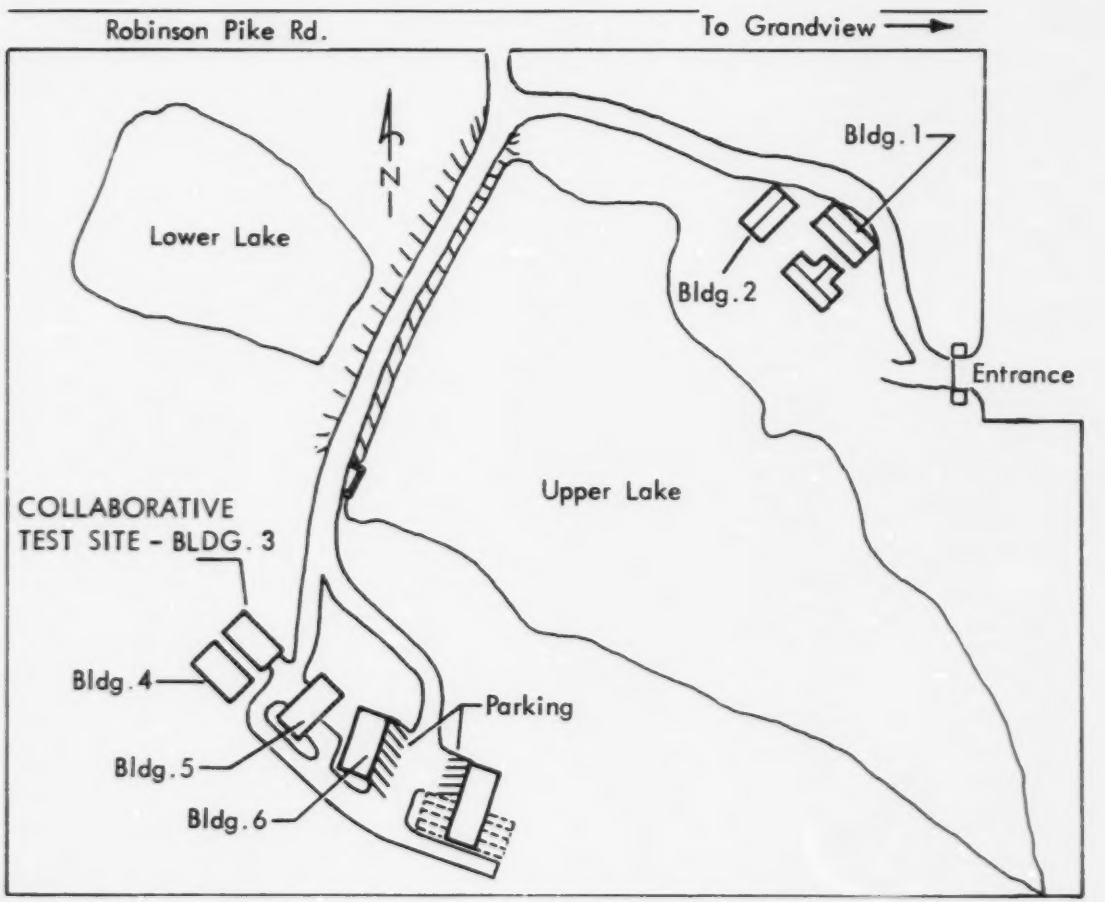
Absorbance of Sample (550 nm) _____ Absorbance of Blank _____

NO_2 Concentration ($\mu g/m^3$) _____ Aliquot (ml) _____

Remarks:

Kansas City
International
Airport
(KCI)
I - 29
I - 35
I - 435
N
KANSAS CITY, MISSOURI
Driving distance
from KCI to
Ramada Inn:
Approximately
35 mi.
87th St.
RAMADA INN
I - 435
71 Highway
Grandview, Missouri

87th St.
RAMADA INN
I - 435
71 Highway
Red Bridge Rd.
112th St.
Grandview Rd.
N
HOLIDAY INN
TRUMAN CORNERS
Garner
Blue Ridge Blvd.
Duck
71 Highway
2nd St.
Main St.
Robinson Pike Rd.
Stop Light
FIELD STATION



DERAMUS FIELD STATION
MIDWEST RESEARCH INSTITUTE
GRANDVIEW, MISSOURI

APPENDIX F

NO_2, AMBIENT-AIR SAMPLING SYSTEM OPERATION DATA: TEST LOG SHEETS AND TEST DATA SHEETS

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System operational data are summarized in Tables F-1 through F-4. Readings were taken hourly during the tests and are recorded on the log sheets which are located after Table F-4. The first nine columns of Tables F-1 through F-4 list various readings used in calculating flowrates and spike levels, which are given in columns 10-14. The last six columns list various ambient air conditions at the test site. The venturi and meter flowrates (columns 10-11) are calculated from the calibration equations in Appendix C. Due to the temperature compensation of the dry-gas meter and the above-ambient pressure of the gas stream at these instruments, the flowrates are calculated at 21°C and 760 mm Hg. The readings of the two devices are then averaged (column 12) and the average flowrate is corrected to the temperature and pressure at the sampling ports (column 13). Some of the methods being evaluated with this system are not corrected for temperature and pressure. However, if the spike levels are not calculated at the temperature and pressure existing at the manifold ports, a significant degree of uncertainty enters into any subsequent use of the spike level. The spike level (column 14) is determined from the permeation rates of the permeation tubes used in each test.

Table F-1. RUN NO. 1 TEST DATA

Date / Time	NO_2 Sampling system data: Room temperature (°C)	Barometric pressure (mm Hg)	Flow pressure (mm Hg)	Flow temp. (°C)	Flow-rate meter (ℓ/min)	Venturi pressure reading (mm H_2O)	N_2 carrier flowrate (cc/min)	Permeation tube temp. (°C)	Calculated flowrates and spike levels: Flowrate: Venturi to 21° +760 mm Hg (ℓ/min)	Flowrate: Meter to 21° +760 mm Hg (ℓ/min)	Average flowrate to 21° +760 mm Hg (ℓ/min)	Average flowrate: Ambient[a] (ℓ/min)	Spike level ambient[a] ($\mu g/m^3$)	Ambient conditions: NO background ($\mu g/m^3$)	NO_2 background ($\mu g/m^3$)	Outdoor temp. (°C)	Wind speed (m/sec)	Wind direction	Relative humidity (%)
4-29-74																			
1120	22.5	741	8	22.0	56.1	241	200	25.0	56.2	56.5	56.3	58.0	95.2	20	90	15.5	4	NNE	100
1230	22.0	741	8	21.4	56.9	248	200	24.9	57.2	57.3	57.2	58.8	93.9	20	80	15.5	4	E	100
1330	21.0	741	8	21.0	57.0	247	200	24.9	57.1	57.4	57.2	58.7	94.0	10	10	17.0	6	E	95
1430	22.0	741	8	21.2	57.3	253	200	25.0	57.8	57.7	57.7	59.3	93.1	10	20	17.5	6	NE	90
1530	23.0	741	8	22.0	57.2	251	200	25.0	57.4	57.6	57.5	59.2	93.2	10	10	19.0	7	NE	85
1630	22.0	741	8	22.0	57.6	253	200	25.0	57.7	58.0	57.8	59.5	92.7	10	10	19.5	7	SE	85
1730	22.0	741	8	22.0	57.5	254	200	25.0	57.8	57.9	57.8	59.5	92.7	10	10	19.0	5	SE	85
1830	22.0	741	8	22.0	57.5	255	200	25.0	57.9	58.0	57.9	59.6	92.5	20	20	19.5	0	E	80
1930	22.0	741	8	22.0	58.1	257	200	25.0	58.1	58.5	58.3	60.0	91.9	15	15	17.0	0	E	80
2030	22.0	741	8	22.0	57.4	234[b]	200	25.0	55.3[b]	-	55.3[b]	56.9	97.0	10	10	16.0	0	E	84
2130	22.0	741	8	22.0	57.1	237[b]	200	25.0	55.7[b]	-	55.7[b]	57.3	96.3	10	20	15.5	0	E	89
2230	22.0	741	8	22.0	58.5	267	200	25.0	59.4	58.9	59.1	60.8	90.7	10	50	15.0	0	E	95
2330	22.0	741	8	21.5	56.9	248	200	24.95	57.1	57.3	57.2	58.8	93.9	10	50	14.5	0	NE	100
4-30-74																			
0030	21.0	741	8	21.0	54.6	235	200	24.95	55.6	55.0	55.3	56.7	97.3	10	50	14.0	0	E	90
0130	22.0	741	8	21.5	57.2	255	200	25.0	58.0	57.6	57.8	59.4	92.9	10	50	14.5	0	NE	95
0230	22.5	741	8	21.5	57.4	251	200	25.0	57.5	57.8	57.6	59.2	93.2	30	60	14.0	0	NW	95
0330	22.0	741	8	21.5	56.2	242	200	25.0	56.4	56.6	56.5	58.0	95.1	10	50	13.5	6	N	89
0430	22.0	741	8	21.5	56.7	243	200	25.0	56.5	57.1	56.8	58.4	94.5	10	40	12.5	7	NW	90
0530	22.0	741	8	21.5	56.2	240	200	25.0	56.2	56.6	56.4	57.9	95.3	10	30	11.0	8	N	84
0630	22.0	741	8	21.5	55.0	239	200	25.0	56.0	55.4	55.7	57.2	96.4	10	20	10.5	7	N	76
0730	22.0	741	8	21.5	57.5	255	200	25.0	58.0	57.9	57.9	59.5	92.7	10	40	11.0	5	NW	77
0830	22.5	742	8	22.0	56.7	252	200	25.0	57.6	57.2	57.4	59.0	93.6	30	40	13.9	7	NW	70
0930	22.0	743	8	22.3	56.5	248	200	25.0	57.1	57.0	57.1	58.6	94.1	30	40	16.0	7	NW	70
1030	22.5	743	8	22.4	56.1	245	200	25.0	56.8	56.6	56.7	58.3	94.7	40	50	20.6	5	N	61
1120	23.0	743	8	22.4	56.0	244	200	25.0	56.6	56.5	56.6	58.1	94.9	30	40	19.0	6	NE	53
Average									57.1	57.1	57.1	58.7	94.1	16	36				

a/ Temperature and pressure at sampling ports.
b/ Flow variation during this period--estimated average flowrate.

Table F-2. RUN NO. 2 TEST DATA

	NO_2 Sampling system data								Calculated flowrates and spike levels					Ambient conditions					
									Flowrate		Average flowrate								
Date Time	Room temperature (°C)	Barometric pressure (mm Hg)	Flow pressure (mm Hg)	Flow temp. (°C)	Flow rate meter (ℓ/min)	Venturi pressure reading (mm H_2O)	N_2 carrier flowrate (cc/min)	Permeation tube temp. (°C)	Venturi to 21° +760 mm Hg (ℓ/min)	Meter to 21° +760 mm Hg (ℓ/min)	To 21° +760 mm Hg (ℓ/min)	Ambient[a/] (ℓ/min)	Spike level ambient[a/] ($\mu g/m^3$)	NO background ($\mu g/m^3$)	NO_2 background ($\mu g/m^3$)	Outdoor temp. (°C)	Wind speed (m/sec)	Wind direction	Relative humidity (%)
4-30-74																			
1207	22.0	743	8	22.0	57.0	253	600	25.0	57.8	57.5	57.7	59.2	196.0	10	20	20.0	4	NE	51
1300	22.5	743	8	22.5	56.8	249	600	25.0	57.2	57.3	57.3	58.9	197.0	10	40	20.5	4	NE	50
1400	23.5	743	8	22.5	56.7	250	600	25.05	57.3	57.2	57.3	58.9	196.9	0	20	21.0	6	N	45
1500	23.5	743	8	22.8	56.2	246	600	25.02	56.8	56.7	56.8	58.4	198.5	0	20	18.0	5	NW	45
1600	22.0	742	8	22.8	56.2	249	600	25.0	57.1	56.6	56.9	58.6	197.9	0	20	19.1	4	NE	45
1700	23.0	742	8	22.8	56.5	248	600	25.05	57.0	56.9	57.0	58.7	197.6	0	20	20.5	3	N	44
1800	23.0	742	8	22.8	57.4	253	600	25.05	57.6	57.9	57.7	59.5	195.0	0	30	20.5	3	N	42
1900	23.5	742	8	22.5	56.2	246	600	25.0	56.8	56.6	56.7	58.4	198.6	0	40	19.5	2	N	41
2000	22.0	742	8	22.1	56.5	250	600	25.0	57.3	56.9	57.1	58.8	197.4	0	60	16.0	0	N	48
2100	22.0	742	8	22.1	56.1	244	600	25.0	56.6	56.5	56.6	58.2	195.4	10	110	11.5	0	N	62
2200	22.0	742	8	21.5	55.3	238	600	25.0	56.0	55.7	55.9	57.3	202.3	0	65	11.0	0	N	65
2300	22.0	742	8	21.5	55.2	236	600	25.0	55.8	55.6	55.7	57.1	202.9	0	60	10.4	0	N	65
2400	22.0	742	8	21.5	56.2	247	600	25.0	57.1	56.6	56.9	58.4	198.7	0	45	9.0	0	N	70
5-1-74																			
0100	22.0	742	8	21.5	58.8	261	600	25.0	58.8	59.3	59.0	60.6	191.5	0	30	9.0	0	N	67
0200	22.5	742	8	21.5	58.6	271	600	25.0	60.0	59.1	59.5	61.1	189.9	0	20	8.0	0	N	70
0300	22.5	742	8	22.0	58.0	268	600	25.0	59.6	58.5	59.0	60.6	191.3	0	40	8.5	0	N	65
0400	22.5	742	8	22.0	57.6	264	600	25.0	59.1	58.1	58.6	60.2	192.7	0	10	8.5	0	N	65
0500	22.5	742	8	21.5	57.9	264	600	25.0	59.2	58.4	58.8	60.3	192.4	0	0	7.5	0	N	70
0600	22.5	742	8	21.5	56.6	254	600	25.0	58.0	57.1	57.5	59.0	196.6	0	10	6.5	0	N	70
0700	23.0	742	8	22.0	56.2	244	600	25.0	56.6	56.6	56.6	58.2	199.2	0	40	9.0	0	N	71
0800	23.0	743	8	22.0	56.0	245	600	25.0	56.8	56.5	56.7	58.2	199.4	40	90	15.0	0	S	82
0900	22.5	743	8	22.5	55.7	240	600	25.0	56.1	56.2	56.2	57.8	200.8	20	70	18.8	2	SE	68
1000	22.0	742	8	22.3	55.8	242	600	25.0	56.3	56.2	56.3	57.9	200.2	10	30	19.1	3	SE	60
1100	22.0	740	8	22.5	55.2	236	600	25.0	55.4	55.5	55.5	57.2	202.5	0	10	24.5	7	S	52
1207	22.0	741	8	22.4	55.2	236	600	25.0	55.5	55.6	55.5	57.2	202.6	0	10	19.2	8	S	52
Average									57.3	57.0	57.2	58.7	197.3	4	36				

a/ Temperature and pressure at sampling ports.

Table F-3. RUN NO. 3 TEST DATA

	NO_2 sampling system data								Calculated flowrates and spike levels					Ambient conditions					
									Flowrate		Average flowrate								
Date Time	Room temperature (°C)	Barometric pressure (mm Hg)	Flow pressure (mm Hg)	Flow temp. (°C)	Flow-rate meter (ℓ/min)	Venturi pressure reading (mm H_2O)	N_2 Carrier flowrate (cc/min)	Permeation tube temp. (°C)	Venturi to 21° +760 mm Hg (ℓ/min)	Meter to 21° +760 mm Hg (ℓ/min)	To 21° +760 mm Hg (ℓ/min)	Ambient[a] (ℓ/min)	Spike level ambient[a] ($\mu g/m^3$)	NO back-ground ($\mu g/m^3$)	NO_2 back-ground ($\mu g/m^3$)	Out-door temp. (°C)	Wind speed (m/sec)	Wind direction	Relative humidity (%)
5-1-74																			
1239	22.0	741	8	22.0	54.3	230	200	25.0	54.9	54.7	54.8	56.4	56.6	0	0	20.4	10	S	48
1330	24.5	740	8	23.8	53.4	226	200	25.1	54.0	53.7	53.8	55.8	57.1	0	0	21.0	9	SE	36
1430	25.5	740	8	25.0	54.8	236	200	25.1	55.0	55.1	55.0	57.3	55.7	0	0	21.1	10	S	39
1530	26.0	739	8	25.7	56.2	249	200	25.3	56.3	56.4	56.4	58.9	54.2	0	0	20.9	8	SE	42
1630	22.0	739	8	22.5	57.6	258	200	25.1	58.0	57.8	57.9	59.9	53.3	0	10	21.5	6	SE	47
1730	22.0	739	8	22.2	56.7	250	200	25.0	57.1	56.9	57.0	58.9	54.2	0	10	20	7	SE	45
1830	22.0	739	8	22.0	57.5	253	200	25.0	57.5	57.7	57.6	59.5	53.6	0	20	20	6	SE	45
1930	22.0	738	8	22.0	57.2	255	200	25.0	57.7	57.3	57.5	59.4	53.7	0	20	17.5	2	SE	47
2030	22.0	738	8	21.5	55.3	241	200	25.0	56.1	55.4	55.8	57.5	55.4	0	30	15.5	2	E	50
2130	22.0	738	8	21.5	57.2	255	200	25.0	57.8	57.3	57.6	59.4	53.7	0	20	14.5	0	E	58
2230	22.0	738	8	21.5	58.5	262	200	25.0	58.6	58.7	58.6	60.5	52.7	0	0	13.5	3	S	61
2330	22.0	738	8	21.5	58.4	264	200	25.0	58.9	58.6	58.7	60.6	52.7	0	0	12.5	5	SE	65
5-2-74																			
0030	22.0	738	8	21.5	59.1	274	200	25.0	60.1	59.3	59.7	61.5	51.9	0	50	11.5	4	E	61
0130	22.0	738	8	21.5	57.4	264	200	24.9	58.9	57.5	58.2	60.0	53.1	0	10	11.0	0	SE	61
0230	22.0	737	8	21.5	57.5	263	200	24.9	58.7	57.6	58.1	60.0	53.1	0	30	11.0	0	S	76
0330	22.0	735	8	21.5	57.9	258	200	25.0	57.4	57.8	57.9	59.9	53.2	0	20	9.5	4	E	61
0430	22.0	734	8	21.5	58.0	259	200	25.0	57.9	57.8	57.9	60.0	53.1	0	0	9.5	0	E	61
0530	22.0	734	8	21.5	56.0	245	200	25.0	56.2	55.8	56.0	58.1	54.9	0	0	9.0	0	E	61
0630	21.0	732	8	21.5	56.5	249	200	24.9	56.6	56.2	56.4	58.6	54.4	0	10	7.5	0	E	88
0730	22.0	732	8	21.5	55.8	242	200	24.9	55.7	55.5	55.6	57.8	55.1	0	10	10.5	0	E	88
0830	21.5	732	8	22.0	55.0	238	220	25.0	55.2	54.7	54.9	57.2	55.7	20	50	14.2	0	E	88
0930	22.0	732	8	22.3	56.1	243	200	25.0	55.7	55.8	55.7	58.1	54.9	10	70	16.5	0	NE	76
1030	22.0	732	8	22.6	55.1	239	200	25.0	55.2	54.8	55.0	57.4	55.6	0	30	18	0	E	78
1130	22.0	732	8	22.5	55.9	245	200	25.0	55.9	55.6	55.7	58.2	54.8	0	20	20.5	3	E	79
1239	21.9	732	8	22.5	55.8	243	200	25.0	55.7	55.5	55.6	58.0	55.0	0	10	23.9	2	S	75
Average									56.9	56.5	56.7	58.6	54.3	1	17				

a/ Temperature and pressure at sampling ports.

Table F-4. RUN NO. 4 TEST DATA

Date Time	NO_2 sampling system data: Room temperature (°C)	Barometric pressure (mm Hg)	Flow pressure (mm Hg)	Flow temp. (°C)	Flow-rate meter (ℓ/min)	Venturi pressure reading (mm H_2O)	N_2 carrier flowrate (cc/min)	Permeation tube temp. (°C)	Calculated flowrates and spike levels: Flowrate: Venturi to 21° +760 mm Hg (ℓ/min)	Flowrate: Meter to 21° +760 mm Hg (ℓ/min)	Average flowrate: To 21° +760 mm Hg (ℓ/min)	Average flowrate: Ambient[a/] (ℓ/min)	Spike level ambient[a/] ($\mu g/m^3$)	Ambient conditions: NO background ($\mu g/m^3$)	NO_2 background ($\mu g/m^3$)	Outdoor temp. (°C)	Wind speed (m/sec)	Wind direction	Relative humidity (%)
5-2-74																			
1304	21.1	732	8	22.5	57.7	257	800	25.0	57.3	57.4	57.4	59.9	298.4	0	10	22.9	4	S	66
1400	22.2	731	8	22.5	57.4	259	800	25.0	57.5	57.0	57.3	59.8	298.5	0	0	22.3	5	S	71
1500	22.1	731	8	22.5	57.3	251	800	25.0	56.5	56.9	56.7	59.3	301.3	0	0	20.5	4	S	71
1600	22.1	731	8	22.5	57.5	255	800	25.0	57.0	57.1	57.1	59.6	299.5	0	0	21.0	6	SE	64
1700	22.0	731	8	22.5	56.8	249	800	25.0	56.3	56.4	56.4	58.9	303.2	0	0	21.5	6	SE	64
1800	22.0	731	8	22.5	56.0	238	800	25.0	55.0	55.6	55.3	57.8	308.9	0	30	21.5	5	SE	64
1900	22.0	731	8	22.0	57.6	250	800	25.0	56.5	57.2	56.9	59.3	301.1	0	20	20.5	6	SSE	67
2000	22.0	731	8	22.0	56.7	254	800	25.0	57.0	56.3	56.7	59.1	302.1	0	20	18.5	3	SSE	75
2100	22.0	731	8	22.0	57.5	256	800	25.0	57.2	57.1	57.2	59.6	299.4	0	50	16.5	2	SSE	84
2200	22.0	731	8	22.0	57.4	254	800	25.0	57.0	57.0	57.0	59.5	300.3	0	45	16.5	0	SE	84
2300	22.0	731	8	21.5	56.2	240	800	25.0	55.4	55.8	55.6	57.9	308.2	0	50	16.5	0	SE	84
2400	22.0	731	8	21.5	55.9	236	800	25.0	54.9	55.5	55.2	57.5	310.4	5	60	15.5	0	SE	84
5-3-74																			
0100	22.0	731	8	21.5	57.0	253	800	25.0	57.0	56.6	56.8	59.1	301.9	0	20	14.5	0	S	84
0200	21.5	733	8	21.5	57.5	256	800	25.0	57.5	57.3	57.4	59.6	299.7	0	40	14.5	14	S	80
0300	21.0	735	8	21.5	58.1	267	800	25.0	59.0	58.0	58.5	60.6	294.8	0	10	13.0	11	S	89
0400	22.0	736	8	21.5	59.4	270	800	25.0	59.4	59.4	59.4	61.5	290.8	0	0	12.0	7	N	84
0500	22.0	736	8	21.5	57.0	264	800	25.0	58.7	57.0	57.8	59.8	298.5	0	0	10.0	8	N	82
0600	22.5	736	8	21.5	55.0	244	800	25.0	56.3	55.0	55.6	57.5	310.2	0	0	9.5	11	N	71
0700	22.5	737	8	21.5	53.8	240	800	24.95	55.9	53.9	54.8	56.7	314.4	0	10	9.5	9	N	70
0800	22.5	740	8	22.0	54.9	238	800	25.0	55.8	55.1	55.5	57.2	312.3	0	20	12	7	N	76
0900	22.9	740	8	22.0	56.1	245	800	25.0	56.6	56.4	56.5	58.2	306.7	0	10	20.6	9	N	70
1000	22.1	741	8	22.0	56.4	250	800	25.0	57.3	56.8	57.0	58.7	304.2	0	10	19.0	6	N	70
1100	22.1	741	8	22.2	57.3	255	800	25.0	57.9	57.7	57.8	59.5	300.2	0	10	21.5	10	N	52
1200	22.0	741	8	22.1	58.0	263	800	25.0	58.4	58.4	58.6	60.3	296.0	0	20	17.0	8	N	48
1300	21.2	740	8	21.8	57.6	256	800	25.0	58.0	57.9	57.9	59.7	299.1	0	20	16.4	6	N	40
Average									57.0	56.8	56.4	58.1	302.4	0	18				

a/ Temperature and pressure at sampling p[illegible].

LOG SHEET *Run # 1*

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE 4-29-74																									
TIME	1120			1430	1530	1630	17.30	8.30	19.30													8:30	9:30	10:30	11:20
OUTDOOR TEMP.	15.5	15.5	17	17.5	19	19.5	19	19.5	11	16	15.5	15	14.5	14	14.5	14	13.5	12.5	11.0	10.5	11.0	13.9	16.0	20.6	19.0
WET BULB	61	61	62	62	62	62	62	61	61			61	61	63	62	62	60	62	59	51	53	49	53	51	51
DRY BULB	61	61	63	64	55	65	65	64	64			61	61	65	63	63	62	64	62	55	57	54	55	58	60
REL. HUMIDITY	100	100	95	90	85	85	85	80		41	39			50	95	55	85	90	94		77	70	70	61	53
BAR. PRESSURE	74.08	74.09	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	74.25	74.27	74.28	74.29
WIND SPEED	1.4 v	1.6 v	2.4	2.5	2.6	2.6	2		.1	.2	.1	.1	.1	.1	.1	.2	2.2	2.8	3.2	2.8	1.8	2.7	2.7	2.0	2.2
WIND DIRECTION	NNE	E	E	NE	NE	SE	SE	E	E	E	E	E	NE	E	NE	NNE	N	NW	N	N	NW	NW	NW	N	NE
POWER LIGHTS	OK	OK	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
LEAKS PERMEATION ASSEMBLY	N/A	N/A	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BATH TEMP.	25	24.9	24.9	25.0	25.0	25.0	25.0	25.0					24.95	24.95	25.0	25.0	25.0	25.0				25.0	25.0	25.0	25.0
ROTAMETERS - 1	95	96	96	95	95	95	95		95	95	95	95	95	95	95	95	95	95	95	95	95	94	94	94	94
2																									
3																									
4																									
N_2 PRESSURE	1100	1100	1100	1060	1050	1060	1060	1060	990	990	990	990	990	910	900	890	950	880	870	810	800	800	790	780	740
RECORDER 1 - PAPER	OK	OK	✓	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓		✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

LOG SHEET

Side 2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
TIME	1120	1230	1330	1430	1530	1630	17.3[illegible]	8:30	19:30	[illegible]	[illegible]	[illegible]	[illegible]	0:30	1:30	2:30	3:30	4:30	5:30	6:30	7:30	8:30	9:30	10:30	11:20
NO_2 ANALYZER - PAPER	OK	OK	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	OK	OK	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE	26	25	25	25	26	25	[illegible]	[illegible]	25	[illegible]	[illegible]	[illegible]	[illegible]	25	25	25	25	25	25	25	25	25	25.5	25.5	25.5
O_2 PRESSURE	20	20	20	20	20	20	[illegible]	[illegible]	20	[illegible]	[illegible]	[illegible]	[illegible]	20	20	20	20	20	20	20	23	20	20	20	20
Base UNSPIKED NO	12	12	11	11	11	11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	11	11	13	11	11	11	11	11	13	13	14	13
NO_2	19	18	11	12	11	11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	15	15	16	15	14	13	12	14	14	14	15	14
Low SPIKED - NO	11	13	11	11	11	11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	11	11	11	11	11	11	11	11	12	13	14	13
High NO_2	27	30	23	23	22	22	22	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	22	26	27	26	26	27	23	25	25	25	25	25
VENTURI MANOMETER - HI	53.0	53.4	534	537	536	537	537.5	538	538.5	537	536	535	534	528	528	536	531	537	530	529	538	535	534	532	531
LO	28.9	28.6	287	284	285	284	283.5	283	282	[illegible]	[illegible]	278	28.6	29.3	29.3	28.5	29.9	28.9	29.2	29.1	28.3	28.3	28.6	28.7	28.7
VENTURI ΔP																									
INDOOR TEMP.	22.5	22	21	22	23	22	22	22	22	22	22	22	22	21	22	22.5	22	22	22	22	22	22.5	22	22.5	23
GAS FLOW TEMP.	22	21.4	21	21.2	22	22	22	22	22	22	22	22	22	21	21.5	21.5	21.5	21.5	21.5	21.5	21.5	22	22.3	22.4	22.4
GAS FLOW MANOMETER - HI	48.6	49.7	488	488	489	489	489	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	495	495	498	498	487	491	492	488	493	487	486	486
LO	[illegible]	38.0	380	380	379	379	379	378	378	[illegible]	[illegible]	[illegible]	[illegible]	393	397	379	395	381	397	[illegible]	379	379	377	380	379
[redacted] flow reading	0[illegible]53	15[illegible]	301	413	524	651	772	900	[illegible]	130	350	462	521	623	736	857	993	097	217	321	440	552	679.7	799.3	898.3
EXHAUST - U MANIFOLD	OK	OK	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S MANIFOLD	OK	OK	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
INITIALS	RS	RS	GWS	[illegible]	[illegible]	[illegible]	ROIL	OK	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	JAC	JAC	JAC	JAC	JAC	JAC	JAC	JAC	RS	RS	RS	RS
time for 2 rev of gas meter	60.6	59.7	59.6	59.3	59.4	59.0	59.1	59.0	[illegible]	[illegible]	[illegible]	58.2	[illegible]	62.2	59.4	[illegible]	[illegible]	59.7	[illegible]	[illegible]	59.1	59.9	60.1	60.6	60.7

LOG SHEET Run #2

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE	7/24	—												7/25	—										
TIME	12:07	13:00	[illegible]	1500	1600	17:00	18:00	19:00	[illegible]	[illegible]	22:00	23:00	24:00	[illegible]	[illegible]	3:00	[illegible]	5:00	[illegible]	7:00	8:00	9:00	10:00	11:00	12:07
OUTDOOR TEMP.	20.0	20.5	21	19	19.1	20.5	20.5	19.5	16.5	11.5	11	10.4	9	9	8	8.5	8.5	7.5	6.5	9.0	15	18.8	19.1	24.5	19.2
WET BULB	54	53	55	55	55	57	55	54	55	52	50	50	49	53	49	50	50	49	49	51	54	54	55	55	55
DRY BULB	64	63	67	67	67	70	66	67	66	5[illegible]	56	56	54	59	5[illegible]	56	56	54	54	56	57	60	63	65	65
REL. HUMIDITY	51	50	45	45	45	44	42	41	48	62	65	65	70	67	70	65	65	70	70	71	72	68	60	52	52
BAR. PRESSURE	74.30	74.28	743 [illegible]	743	74.24	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	743	74.23	74.21	74.20	74.13
WIND SPEED	1.4	1.5	2.1	1.8	1.3	1	1	[illegible]	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	1.1	2.6	3.4
WIND DIRECTION	NE	NE	NE	NE	NE	N	N	N	N	N	N	N	N	N	N	N	N	N	N		S	SE	SE	S	S
POWER LIGHTS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BATH TEMP.	25.0	25	25.0	25.0	25.0	[illegible]	[illegible]	[illegible]	25	25	25	25	25	25	25	25	25	25	25	25	25.0	25.0	25.0	25.0	25.0
ROTAMETERS - 1	94	94	94	98	98	98	[illegible]	[illegible]	99	99	99	99	[illegible]	99	99	99	99	99	99	99	99	99	99	99	99
✗	[illegible]																								
3	95	95	95	99	99	99	[illegible]	[illegible]	995	100	100	995	99	99	99	99	99	99	99	99	99	100	100	100	100
4	95	94	94	99	99	99	[illegible]	[illegible]	995	995	99.5	99.5	99	95	99	99	99	99	99	99	100	99	100	100	100
N_2 PRESSURE	720	710	700	700	670	650	[illegible]	[illegible]	[illegible]	[illegible]	590	550	520	510	500	500	490	470	470	450	400	420	380	350	320
RECORDER 1 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	—	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	—	✓	✓	✓	✓	✓
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓	[illegible]	[illegible]	✓	✓	[illegible]	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	[illegible]	[illegible]	✓	✓	[illegible]	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

LOG SHEET

Side 2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
TIME	12:27	13:[illegible]	[illegible]	14:30	1600	1730	18:[illegible]	[illegible]	[illegible]	2:[illegible]	22:30	25:00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1[illegible]	10[illegible]	11:[illegible]	12:27
NO_2 ANALYZER - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE	25.5	25.5	[illegible]	[illegible]	25.5	25.5	25.5	25.5	25.5	25.5	25.5	26.[illegible]	25.5	25.5	25.5	25.5	25.5	[illegible]	25.5	25.5	26	25.5	[illegible]	[illegible]	25.5
O_2 PRESSURE	20	20	[illegible]	[illegible]	20	20	[illegible]	[illegible]	20	20	[illegible]	20	20	20	20	20	20	20	20	20	20	20	[illegible]	[illegible]	20
UNSPIKED - NO	[illegible]	11	10	10	10	10	10	10	10	11	10	10	10	10	10	10	10	10	10	10	14	12	11	10	10
NO_2	12	14	12	12	12	12	13	14	16	21	16.5	16	14.5	13	12	14	11	[illegible]	11	11	18	17	13	11	11
SPIKED - NO	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	12	15	11	11	11
NO_2	36	36	38	37	37	37	36	38	385	42	45	40	39	35	35	35	35	34	35	38	40	43	39	36	36
VENTURI MANOMETER - HI	53.6	53.4	53.6	53.3	53.4	53.4	53.7	53.4	53.5	53.2	52.9	52.8	53.3	54.0	54.[illegible]	54.4	54.2	54.2	53.7	53.7	53.4	53.9	53.[illegible]	52.7	52.7
-O	28.3	28.5	28.6	28.7	28.5	28.[illegible]	28.4	28.[illegible]	28.5	28.8	29.1	29.2	28.6	27.9	27.5	27.6	27.6	27.[illegible]	28.3	28.3	28.[illegible]	28.7	28.5	27.1	29.1
VENTURI ΔP																									
INDOOR TEMP.	22	22.5	22.5	23.5	22	23	23	23.5	22	22	22	22	22	22	22.5	22.5	22.5	[illegible]	22.5	23	23	22.5	22	22	22
~~GAS~~ FLOW TEMP.	22.5	22.5	22.5	22.5	22.8	[illegible]	22.8	[illegible]	[illegible]	[illegible]	[illegible]	21.5	[illegible]	21.5	21.5	22.0	22.[illegible]	[illegible]	21.5	22	22	22.5	[illegible]	22.5	22.4
GAS FLOW MANOMETER - HI	48.7	48.7	48.7	48.7	48.7	48.7	48.[illegible]	48.7	48.2	48.[illegible]	48.5	48.5	48.6	48.0	48.1	48.1	48.0	48.0	48.[illegible]	48.[illegible]	48.[illegible]	48.5	[illegible]	48.4	48.4
LO	37.7	37.8	[illegible]	38.0	37.8	37.9	37.7	[illegible]	[illegible]	38.[illegible]	38.[illegible]	38.1	38.0	37.7	37.6	37.6	37.7	37.7	37.8	>38.2	38.0	38.[illegible]	[illegible]	[illegible]	38.2
~~GAS FLOW PRESSURE~~ CUFT	772.2	779.3	[illegible]	787	795.0	[illegible]	810	[illegible]	[illegible]	836	850.7	[illegible]	[illegible]	853.0	[illegible]	[illegible]	911	939	952	974	[illegible]	998.[illegible]	[illegible]	773.7	773.9
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	[illegible]	✓	✓	✓	✓	✓	✓	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	✓	✓	✓	✓	✓
S MANIFOLD	✓	✓	✓	✓	✓	[illegible]	✓	[illegible]	✓	✓	✓	✓	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	[illegible]	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
INITIALS	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] / 2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

LOG SHEET Run #3

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE	7/24												7/25												
TIME	12:39	13:39	14:39																				10:39	11:39	12:39
OUTDOOR TEMP.	20.4	21.0	21.1	20.7	21.5			19.5	19	19.5	19.5	12.5	11.5	11.0	11.0								31	30.5	23.9
WET BULB	55	55	55	55	57		55	53	53	53		50	51	50		50		51	51				56	60	66
DRY BULB	70	70	67	68	69		67	64		60	58	50	56	57		57		59					60	57	65
REL. HUMIDITY	48	56	39	42	47		45	47		58	61	85	61			61	61	61					78	79	75
BAR. PRESSURE	29.38	29.44	29.43	29.37	29.47								29.38										29.32	29.33	29.318
WIND SPEED	4.4	3.6	4.4	3.3	2.2					0	1	2	1.4	0	0	1.0	0	0	0	0	0	0	0	1.0	0.4
WIND DIRECTION	S	SE	S	SE	SE	S	SE	SE	E	E	S	E	E	SE	S	E	E	E	E	E	E	NE	E	E	S
POWER LIGHTS	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BATH TEMP.	25.0	25.1	25.1	25.2	25.1							25	25	24.9		24.5							25.0		25.0
ROTAMETERS - ✗																									
✗																									
3	100	79	100	99									99	95	99								78	78	98
✗																									
N_2 PRESSURE	320	310		292										650									500		480
RECORDER 1 - PAPER	✓	✓		✓	✓		✓	✓				✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓
OPERATION	✓	✓		✓	✓		✓	✓				✓	✓	✓	✓	✓	✓	✓	✓	✓			✓	✓	✓
RECORDER 2 - PAPER	✓	✓		✓	✓			✓				✓		✓	✓					✓			✓	✓	✓
OPERATION	✓	✓		✓								✓	✓	✓	✓								✓	✓	✓

LOG SHEET

Side 2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
TIME	12:39	13:39	14:39	15:39	16:39	17:39	18:39	19:39	20:39	21:39	22:39	23:39									8:39	9:39	10:39	11:39	12:39
NO_2 ANALYZER - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE	25.5	25.5	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.6	25.3	25.3	25.3
O_2 PRESSURE	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20.1	20.1
UNSPIKED - NO	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
NO_2	10	10	10	10	11	11	11	11	11	11	11	10	15	11	13	12	13	13	13	13	12	12	13	12	11
SPIKED - NO	10	10	10	11	11	11	11	11	10	10	10	10	10	13	10	10	10	10	10	10	12	11	11	10	10
NO_2	17	18	17	17	17	17	17	17	19	19	19	17	16	17	17	17	18	17	17	18	22	22	21	18	17
VENTURI MANOMETER - HI	52.4	52.1	52.6	53.3	53.2	53.5	53.6	53.7	53.2	53.7	54.1	54.2	54.7	54.7	54.1	53.9	53.9	53.4	53.4	53.2	52.5	53.0	52.8	53.1	53.0
LO	29.4	29.5	29.0	28.4	25.1	28.5	28.3	28.2	28.9	28.2	27.9	27.4	27.3	27.9	27.8	28.1	28.1	27.7	27.5	27.5	27.3	28.7	28.9	28.6	28.7
VENTURI ΔP																									
INDOOR TEMP.	22	24.5	25.5	26.0	22	22	22	22	22	22	22	22	22	22	22	22	22	22	21	22	21.5	22.5	22	22	21.9
GAS FLOW TEMP.	22.9	23.5	25.9	25.7	25.6								15	21.5	21.5	21.5	21.5	21.5	21.5	21.5	22.5	22.5	22.6	22.5	22.5
GAS FLOW MANOMETER - HI	48.3	48.1	48.4	48.6	48			48.2	48.5	48.7	48.9	48.3	48.1	48.1	48.8	48.8	48.8	48.8	48.7	48.7	48.7	48.1	48.4	48.5	48.5
LO	38.2	38.3	38.3	37.5	37.1			37.6	38.1	37.8	37.8	37.4	37.4	37.7	37.6	37.9	37.9	37.9	37.9	37.8	37.7	37.7	37.9	37.7	37.9
~~GAS FLOW PRESSURE~~ CU FT	736.0	833.4	1478.2	2673.8	442	5[illegible]	641	755	573	[illegible]	1201	2236	362	459	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	373	456.9	575.3	694.1	832.3
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
INITIALS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS	RCS
1/2 CU FT	62.0	63.6	62.0	60.4	[illegible]	[illegible]	54.1	[illegible]	59.7	59.1	58.1	58.2	57.5	59.2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	61.3	[illegible]	61.6	60.8	60.9

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LOG SHEET Run #4

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE	5/2/94												5/3/94												
TIME	13:39	1400	15:	16:	17:50	18:0	19:0																		13:04
OUTDOOR TEMP.	22.7	22.7	20.5	21	21	21.5	20.5	18.5	16.5			15.5	15	14.5	13.0	12.0	10.0	9.5	8.5	12		17.0	21.5	17.0	16.4
WET BULB	60	61	61	62	61	62	62	62	61	61	61	61	61	61	59	61	58	58					53		49
DRY BULB	67	67	67			70	69	67	64			64	66	65	61		67	58					59	61	61.5
REL. HUMIDITY	66	71	71	64	61	69	67	75	84		84	84	84	80	89	84	82	71	70	76	70		52	48	40
BAR. PRESSURE	73.15	73.12	73.10	73.08	73.8	73.08	73.01	73.0	73.09	73.1		73.14	73	73.3	73.5	73.6	73.6	73.7	73.7	73.9	74.04	74.26	74.10	74.10	74.00
WIND SPEED	1.4	1.7	1.4	2.1	2.1	2.0	2.2	1.8	0.6	0		0	0	6.0	9.6	2.7	3.4	4.8	3.8	3.0	3.5	2.3	4.0	3.5	2.5
WIND DIRECTION	S	S	S	SE	SE	SE	SSE	SSE	SSE			SE	S	N	N	N	N	N	N	N	N	N	N	N	
POWER LIGHTS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BATH TEMP.	25.0	25.0	25.0	25.0	25	25	25		25													25.0	25.0	25.0	25.0
ROTAMETERS - 1	97	97	97	97	97	97	97	97	97	97		97	97	97	97	97	97	97	97	97	97	97	97	97	97
2	99	98	99	98	98							99	99	99	95	99	99	99		99	98	98	97	95	97
3	98	95	98	95	98	98	98	98					97	99	95	98	98			98	100	98	98	100	98
4	98	97	98	98	98	98								99		98	98			97	97	97	97	97	98
N_2 PRESSURE	460	45	430	410	400	390	380	360	340																2010
RECORDER 1 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓				✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓				✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓		✓	✓				✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

Dry bulb sticking at 5 °F. Temp. taken from

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LOG SHEET

Side 2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
TIME																									
NO_2 ANALYZER - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓						
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE																									
O_2 PRESSURE																									
UNSPIKED - NO	10				10		10	10	10	10				10	10	10	10	10	10	10				10	10
NO_2	11				10		12			14	15	12		14	11	10	10		11		11	11	12	12	
SPIKED - NO	10	10	10	11	11	11	11	11	10	11		11	11	11	11	10	10	11		11	11	11	11	11	10
NO_2	47	46	47	47	47	49	50		49	51		53	50	48	48	47	46	47	52			41	45	50	50
VENTURI MANOMETER - HI	527	538	534	536	533		534	536	537			52.7	536	537	543	544	541	531					53.6	54	53.6
LO	28.3	27.9	28.3	28.1	26.4		28.4	28.3	28.1			29.1	28.3	28.1	27.6	27.4	27.7	25.7				28.1		27.7	28.1
VENTURI ΔP																									
INDOOR TEMP.	21.1	22.2		22.1			22	22	22				22	21.5	21	22	22								
GAS FLOW TEMP.	22.5	22.5		22.5			22	22	22	22				21.5	21	21.5	21.5	21.5	21.5	22		22.2	22.2	22.1	21.8
GAS FLOW MANOMETER - HI	48.8	47.8	49	48.7		48.5	48.6	48.6	48.7	48.6															48.7
LO	37.6	37.4	37.7	37.6	37.2	37.8	37.7	37.7	37.6	37.7				37.5	37.5	37.5		37.4							37.6
~~GAS FLOW PRESSURE~~ CU FT	782.9	796.1	815.6	828.3	376	497	612	739	846	973															791.3
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
INITIALS																									
Sa.../2 CU FT	589			591			591	591	592	592	596	596	595	595	594	594	594	594	595	596	596	596	596	596	RCS 59.0

APPENDIX G

COLLABORATORS' COMMENTS

During the orientation of the collaborators at the field site, they were asked to provide MRI with comments on the method writeup, problem areas, etc. Eight of the 10 responded with comments which are given below by collaborator code.

Collaborator B

The scatter in the data is considerable for some of the runs. I ran a few duplicates, as indicated, which gave a nearly identical pattern in the scatter. It would seem to me that the problem was in the sampling end of the test.

Several explanations have occurred to me. A leak in the sampling system at the point of attachment to the NO_2 system would give low results. In addition, if the scrubbing action of the bubblers was inadequate, this would also give a low result. Both seem to me to be possible explanations for the apparently low values for some of the samples.

I reran the calibration curve. There was a slight change over the old one, and the values for the new curve were used in the calculations.

Collaborator C

Absorbing solution in samples Sets 3 and 4 had mold growing in the liquid when received.

Collaborator D

The water lost by evaporation during sampling was replaced in the absorption tubes before they were packed for shipment. After shipping, 10 of the tubes had lost some liquid. The tubes were sealed in plastic bags which had the liquid in droplets all over the inside. The caps on the tubes seemed tight and there were no visible cracks in any tube. I could not tell if the liquid had evaporated out of the tubes because of heat, or if it had spilled out.

Two of the low volume tubes in the first days run were brought up to 50 ml using a buret to measure the amount of water needed. Analysis showed these two tubes had lower concentrations than their companion tubes. Recalculating the concentrations, taking into account how much the solutions

had been diluted, increased the concentrations to agree with their companion solutions. Therefore, the remaining low volume tubes were analyzed without making them up to 50 ml. All the low volume samples are designated on the data sheets.

Collaborator F

Analyses: Duplicate aliquots were run on the 24-hr samples and triplicates on the MRI samples. The calibration curve was run in triplicate. Although the calibration curve at low NO_2 concentrations is not linear, the variations at these points are within the limits of replicate analyses.

For the 24-hr samples, the net sample absorbance ranged from 0.034 to 0.784 absorbance units. Based on 24 duplicate analyses the pooled standard deviation of the mean for duplicate analysis is 0.0038 absorbance units. This represents 0.0075 μg NO_2/ml of absorber solution, or for samples of approximately 0.3 m^3 of air, about 1.3 μg NO_2/m^3 of air. For the spiked samples, this represents a possible error of 1-4% due to the color development and absorbance measurement. For the unspiked samples, this could account for errors of 10-20%.

The spiked samples from Port 8 are lower than the other replicates in each case. For Runs 1 and 2 the differences are substantial, only marginal in Run 3, and insignificant in Run 4. The maximum relative error associated with the air flow measurements would be about 2%. The maximum error expected in the analysis (including instrumental error) would be about 3 $\mu g/m^3$ or about 3% for Run 1 and 1.5% for Run 2. Thus, for Runs 1 and 2, the samples from Port 8 are obviously outliers. These are almost certainly due to a leak in the sample train, probably at the connection to the sample port. All other runs show good agreement, well within the expected errors.

Comments: We have not encountered any significant difficulties in applying this method and we plan to use it as a cross-check with the continuous chemiluminescence detector. The drawback to the method is the limited shelf-life of the prepared solutions, plus the difficulty in obtaining o-methoxyphenol of the specified grade.

Collaborator G

The samples collected and unknowns given were analyzed in strict accordance with the method. The only modification made in the procedure was in the calibration of the rotameter used due to the unavailability of the 1 liter wet test meter required. A bubblemeter was used instead.

The overall method was simple and straightforward. No difficulty was encountered in the analysis.

Collaborator H

All samples were run twice to verify results. Slopes of standard curves were 0.44 and 0.38. This is not the 0.5 slope suggested by the method. Analyses were performed exactly as outlined in the procedure.

Certain problems were experienced in sampling and analysis:

Sampling: Evaporation during sampling resulted in a loss of almost 50% of the fluid in the sampling tubes. This problem was most pronounced on Run No. 1. It was not noticeable in the sodium-arsenite testing.

Calibration: Calibration of flow meters at our laboratory causes a slight variation from flow determined at the test site. A difference of 3,000 ft in elevation and different humidity might be the cause.

Analysis: Odd sized aliquots, such as 2.7 ml of sulfanilamide solution provide means where error might enter in. Standard pipet sizes of 2 or 3 ml would be found in all laboratories, and could be added in a more rapid, accurate and reproducible manner. A change in solution strength would accomplish this change.

It is interesting to note fritted glass bubblers were not allowed because of expense, and "They are not needed." Yet in the method of Continuous Saltzman, paragraph 5, it is noted that NO_2, "Is somewhat difficult to absorb."

Collaborator I

You will notice the slope is less than it should be. I tried a number of times but got approximately the same slope (must be the dye).*

* Subsequent communications have revealed that the poor results were caused by contaminated methanol. See page 41.

Collaborator J

Calibration: Since we did not have a 1-liter wet test meter and the volume to be measured was small, the Fisher-Porter Company rotometer was calibrated with a 250-ml soap bubble meter.

Observations: Upon opening the sample tubes on 14 May prior to analysis, it was noted there was white, flocculent matter in all the tubes of varying amounts. Absorbing reagent used in the test was found to be clear. Tubes taken to the test site but not used were filled with absorbing reagent and observed for clarity--no flocculence was noted. The tubes had not been exposed to light. The absorbing reagent was prepared on 26 April and was 17 days old at the time of analysis. All chemicals used were of the purity specified by the method.

APPENDIX H

ANALYSIS OF VARIANCE INCLUDING COLLABORATOR I

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One collaborator (I) produced useless results, but the analysis of variance with (I) included is presented for completeness. Since (I) observed virtually no NO_2, the average bias with (I) included depends on the level of NO_2. Also, of course, the average bias is much larger with (I) included (-24.6 $\mu g/m^3$ versus -9.5 $\mu g/m^3$). The collaborator variance is 30 times as large when (I) is included.

ANALYSIS OF VARIANCE ((I) INCLUDED)

Source	df	SS	MS	F	EMS
Total	153	465,837.33	-	-	-
C	9	339,435.23	37,715.03	703+	$\sigma_e^2 + 16\ \sigma_c^2$
L	3	23,651.13	7,883.84	147+	$\sigma_e^2 + 4\ \sigma_{cc}^2 + 40\ \sigma_c^2$
CL	27	96,637.49	3,579.17	66+	$\sigma_e^2 + 4\ \sigma_{cc}^2$
Error	114	6,113.08	53.62	-	σ_e^2

COMPONENTS OF VARIANCE

	σ^2 ($\mu g^2/m^6$)	σ ($\mu g/m^3$)
Collaborator	2,353.84	48.52
Level	107.62	10.37
CL	881.39	29.69
Error	53.62	7.32